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New combined phenol/hindered amine photo- and thermal-stabilizers based on toluene-2,4-diisocyanate

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Abstract

Reactions of toluene-2,4-diisocyanate with different phenols and different HAS (hindered amine stabilizers) were used to prepare new combined phenol/HAS. As a phenol 2-*tert*-butyl-4-methoxyphenol (**I**); 2-*tert*-butyl-4-methylphenol (**II**); 2,4-di-*tert*-butyl-6-methylphenol (**III**) and 2,4-di-*tert*-butylphenol (**IV**) were used. HAS represented 4-hydroxy-2,2,6,6-tetramethylpiperidine (**TMP**), 4-hydroxy-1,2,2,6,6-pentamethyl-piperidine (**PMP**), 4-amino-2,2,6,6-tetramethylpiperidine (ATP), 4-*N*-butyl-amino-2,2,6,6-tetramethyl-piperidine (**BATP**) and 4-hydroxy-2,2,6,6-tetramethylpiperidin-*N*-oxyl (**TMP-NO$^{\cdot}$**). Symmetrical phenol–phenol and HAS–HAS were also prepared. The synthesized compounds were tested as light and thermo stabilizers in polypropylene (PP). Non-oxidized as well as partially oxidized PP was used. The stabilizing efficiency depends on the structure of the phenol as well as the HAS. Concerning the phenol structure the best efficiency at photo oxidation was obtained with combined phenol/HAS containing 2,6-disubstituted phenol III for all HAS used. Efficiencies of phenols with just one substituent in the *ortho* position in combined additives were much lower. This difference was rather small in the case of thermo oxidation. Among the HAS the best performance was obtained from derivatives of TMP and PMP in photo oxidation of non-oxidized PP matrix. PMP derivatives in contrast to TMP ones did not stabilized partially oxidized PP very well. The efficiency of combined phenol/HAS was much higher than the efficiency of symmetrical HAS/HAS despite two times higher concentration of the active part in the symmetrical molecules. All combined additives showed very good ability to stabilize PP against thermo-oxidation. The highest efficiency was reached with TMP derivatives—about 12 000 to 14 000 h to reach carbonyl absorption 0.2 at 110 °C.

Keywords: Stabilization; Thermo-oxidation; Photo-oxidation; Combined stabilisers; Phenols; Hindered amines; Polypropylene

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1. Introduction

Polymer materials, especially polyolefins, undergo degradation under the action of light heat and oxygen by a free radical mechanism leading to different oxidation products. This process results in the loss of physical and mechanical properties. The degradation of polymers can be inhibited effectively by the addition of small quantities of stabilizers. A small quantity of processing stabilizers is usually added to prevent the oxidative degradation of polyolefins caused by combined action of shear, heat and oxygen during their melt processing. Phenolic antioxidants often in combination with hindered phosphites are widely used as processing stabilizers for polyolefins [1,2]. They act as scavengers of oxygen-centred alkoxy and peroxy radicals, but they are not able to provide long term light and heat stability [3].

Nowadays hindered amine stabilizers—(HAS) are the most effective long-term light and partial heat stabilizers. Beside the stabilization of polyolefins they find wide application in the protection of various polymer systems of commercial interest [4–6]. They act by a multifunctional mechanism.

The addition of a mixture of a processing stabilizer (phenol and phosphite type) and long-term stabilizer (HAS type) to the polymer is frequently used to prevent the polymer against degradation. Disadvantages of using mixtures of low molecular weight stabilizers are mainly their physical loss, uneven distribution in the polymer matrix and poor compatibility. One way to solve this problem is to use the multifunctional additives with higher molecular weight prepared by the connection of two or more stabilizing structures in one molecule. This combination is expected to improve the

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stabilizing activity by synergistic effects. An elegant method to connect hindered phenol type antioxidants with hindered amines resulting in the higher molecular weight multifunctional stabilizers is their stepwise reaction with di-(or poly)isocyanates [7–9].

In this work we describe the synthesis and stabilization efficiencies of four series of combined phenol/HAS stabilizers derived from four different phenols. In some cases the corresponding stable nitroxyl radicals were prepared as well. To check the positive effect of the combination of phenol and HAS symmetrical phenol–phenol as well as HAS–HAS were also synthesized and their stabilizing efficiencies compared. Toluene 2,4-diisocyanate was used as a coupling agent. In order to test the efficiency of the new type of combined stabilizers for resins obtained from recycling partially oxidized PP powder was used. Partially oxidized PP might be a suitable model for the complex polymer mixture to be recycled.

2. Experimental

2.1. Materials

4-Hydroxy-2,2,6,6-tetramethylpiperidine (**TMP**), 4-hydroxy-1,2,2,6,6-pentamethyl-piperidine (**PMP**), 4-amino-2,2,6,6-tetramethylpiperidine (**ATP**), 4-*N*-butylamino-2,2,6,6-tetramethylpiperidine (**BATP**) and 4-hydroxy-2,2,6,6-tetramethylpiperidin-*N*-oxyl (**TMP-NO**) were supplied by HÜLS. 1,4-Diazabicyclo-[2,2,2]-octane (**DABCO**), 1,8-diazabicyclo-[5,4,0]-undec-7-ene (**DBU**), toluene 2,4-diisocyanate (**TDI**) and phenols 3-*tert*-butyl-4-methoxyphenol (**I**); 2-*tert*-butyl-4-methylphenol (**II**); 2,4-di-*tert*-butyl-6-methylphenol (**III**) and 2,4-di-*tert*-butylphenol (**IV**) were obtained from Merck. Two types of polypropylene powder-Tatren HPF- containing no commercial additives (supplied by Slovnaft, Bratislava, Slovak Republic) were used. The first was fresh, containing no measurable amount of oxidation products. The second one was partially oxidized by storing in air at laboratory temperature for one year.

2.2. Analysis

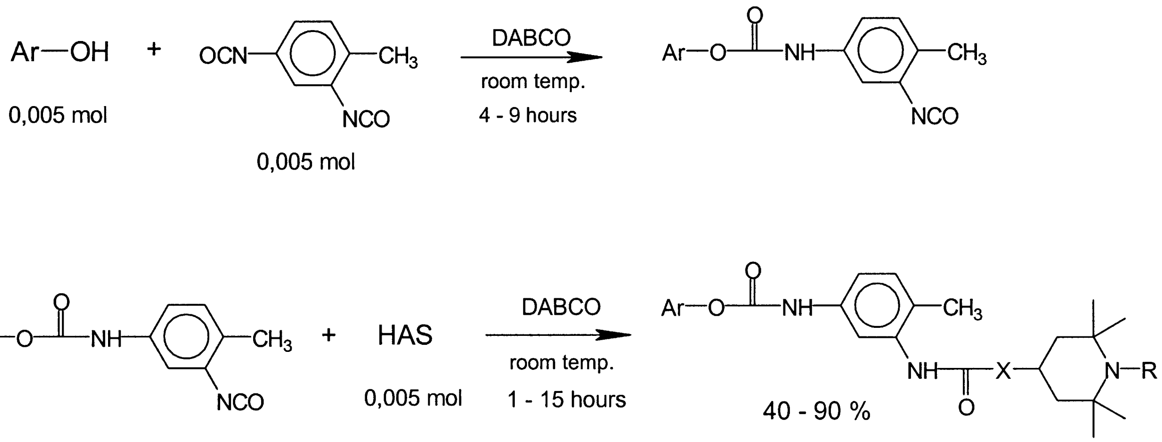
Infrared (IR) spectra were recorded on a Nicolet FT-IR 400 (Germany) spectrometer. Elemental analysis for carbon, hydrogen and nitrogen was performed with CHN-S Elemental Analyzer 1108 (Carlo Erba). ^{1}H-NMR spectra were recorded on a Bruker 300 MHz NMR spectrometer. EPR spectra were measured on a Varian spectrometer. UV spectra were recorded on an M40 spectrometer (C. Zeiss, Jena, Germany).

2.3. Synthesis

Combined phenol/HAS were prepared according to Scheme 1.

To a solution of 0.005 mol of respective phenol (Ar-OH) and 0.005 mol TDI in 20 ml of dry toluene, 50 mg of DABCO was added. Reactions were maintained at room temperatures for 4 h in the first step and 1–15 h in the second step. Second reactant (HAS) was added when isocyanate peak at 2260 cm^{-1} reduced to half in the FT-IR spectrum. The reaction was stopped when the isocyanate peak disappeared completely. White or slightly yellow precipitates appeared by adding n-pentane and removing the solvent from reaction mixture by rotovapor. Products were purified by re-crystallization from mixture of ethyl acetate: *n*-pentane or by column chromatography using as eluent mixtures of ethyl acetate: *n*-pentane from the ratio 1:1 up to pure ethyl acetate. Reaction conditions, time of reactions, yields and melting points of combined phenol/HAS are shown in Table 1.

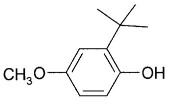
Symmetrical additives were synthesized by the same procedure only the molar ratio of phenols or HAS to TDI was 1.1 to 0.5 mol and DBU instead of DABCO

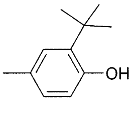


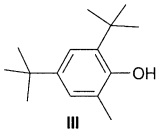
Scheme 1.

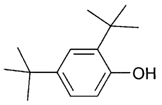
was used as a catalyst. Some data concerning synthesis and the final products are given in Table 2.

Structures of phenols Ar–OH used are as follows:

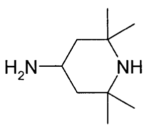

I

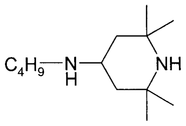

II

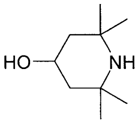

III

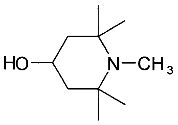

IV

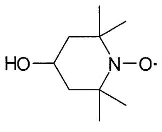
Structures of HAS:


ATP


BATP


TMP


PMP


TMP-NO·

2.4. Sample preparation

All the additives (0.2 wt.%) were solvent blended into the polymer powder using dichloromethane as solvent. After evaporation of the solvent with mixing, the polymer samples were mixed and homogenized in a chamber of a Brabender Plastograph (Duisburg, Germany) at 190 °C for 5 min in air at 40 rpm. The bulk polymer was then pressed into ca 0.1 mm thick films in an electrically heated laboratory press (Fontune, Vlaardingen, Netherlands) at 190 °C for 1 min.

2.5. Photo- and thermo-oxidation

The photo-oxidation was performed on a merry-go-round type set up, using a medium pressure 250 W mercury arc with luminophore envelope (RVL, Tesla Holešovice, Czech Republic) as the source of irradiation. The temperature of photo-oxidation was 30 °C. Thermo-oxidation was carried out in an oven with forced air circulation at 110 °C.

The course of photo- and thermo-oxidation was followed by IR spectroscopy monitoring the increase of carbonyl absorption between 1700 and 1740 cm^{-1}, caused by oxidation products.

Table 1
Experimental conditions, yields and melting points of combined phenol/HAS

Code Name	Phenol	HAS	Temp. (°C)	Reaction time (h)	Yield (%)	Melting point (°C)
ATP I	I	ATP	RT	4+1	89	121–124
ATP II	II	ATP	RT	4+1	58[a]	133–137
ATP III	III	ATP	RT	4+1.5	22[a,b]	153–156
ATP IV	IV	ATP	RT	4+1	41[a]	147–150
BATP I	I	BATP	RT	4+1.5	39[b]	89–93
BATP II	II	BATP	RT	4+1.5	62[a]	86–91
BATP III	III	BATP	RT	4+2	78	105–108
BATP IV	IV	BATP	RT	4+2	64	94–99
TMP I	I	TMP	RT+40	4+3	68[a]	74–77
TMP II	II	TMP	RT+40	4+3	55[a]	79–82
TMP III	III	TMP	RT+40	4+3	87[a]	99–103
TMP IV	IV	TMP	RT+40	4+3	72[a]	81–83
PMP I	I	PMP	RT	4+15	43[b]	88–92
PMP II	II	PMP	RT	4+15	41[b]	100–104
PMP III	III	PMP	RT	4+15	64[a]	101–107
PMP IV	IV	PMP	RT	4+15	58[b]	97–101

[a] Purified by recrystallization.

[b] Purified by column chromatography. Others without this purification.

Table 2
Experimental conditions, yields and melting points of symmetrical additives phenol-phenol and HAS-HAS

Code name	Reaction temp. (°C)	Reaction time (h)	Yield (%)	Purified by	Melting point (°C)
ATP–ATP	40	24	80	–	210–212
BATP–BATP	60	24	74	*n*-Heptane	100–103
TMP–TMP	40	24	87	Acetonitrile	195–197
PMP–PMP	RT	2	91	*n*-Hexane/ethyl acetate	171–173
I–I	110	2	45	Dichloromethane/*n*-hexane	102–104
II–II	Reflux	2	45	Dichloromethane/*n*-hexane	98–100
III–IIII	Reflux	2	77	Dichloromethane/*n*-hexane	148–150

3. Results and discussion

3.1. Synthesis of stabilizers

It is well known that isocyanates can easily react with primary alcohols or amines producing carbamates or ureas [10–13]. Using phenols as well as secondary alcohols requires catalytic conditions. Because of this fact we used 1,4-diazabicyclo-[2,2,2]octane (DABCO) as a catalyst in our synthetic procedure. The reactions of combined phenol/HAS preparations were performed as a one-pot process without isolation of intermediate products i.e. the products of phenol addition to TDI. The end of this first step was easy monitored by FTIR spectroscopy. The characteristic band of the isocyanate group at 2260 cm^{-1} dropped down to the half of its original intensity. After addition of HAS the reaction was finished at complete extinction of isocyanate absorption. The reaction time and the reaction temperature depend on the structure of HAS. Shorter time (1–2 h) was needed for addition of amines ATP and BATP at laboratory temperature. The addition of alcohol—PMP—at the same temperature was much slower and needed 15 h. Increasing temperature to 40 °C in the case of very similar alcohol addition—TMP—resulted in much shorter reaction time —3 h— to complete reaction.

Some of the products received from the reaction were pure enough, some were purified by crystallization and some needed purification by column chromatography. The last two procedures naturally decreased the yields of reactions. Reaction conditions, yields and melting points of pure synthesized compound are given in Table 1. Preparation of symmetrical carbamates containing two phenols or carbamates and ureas containing two HAS in the form of parent amine or stable nitroxyl radical was similar and some characteristics concerning some of these compounds are given in Table 2.

The structure and the purity of all synthesized compounds were proved by elemental analysis, ^{1}H-NMR and FT-IR spectroscopy as well as MALDI-TOF mass spectrometry. FT-IR spectra showed new peaks at 1750 cm^{-1} in the case of carbamates (all phenols, TMA, PMA) and at 1650 cm^{-1} in the case of ureas (ATP and BATP). ^{1}H-NMR spectra besides typical peaks for 2,2,6,6-tetramethylpiperidine ring as well as for aromatic protons contain peaks of N$\underline{\text{H}}$-CO group of ureas and carbamates in the region 6.5–7.2 ppm. In the case of ureas prepared from ATP another N$\underline{\text{H}}$-CO proton showed the peak at 4.6–5.2 ppm. MALDI-TOF mass spectra showed the expected molecular peak for each synthesized compound.

3.2. Photo-oxidation of partially oxidized PP

All synthesized compounds were tested as light and some of them as thermo-stabilizers. To provide the best dispersion in PP matrix additives were first solvent

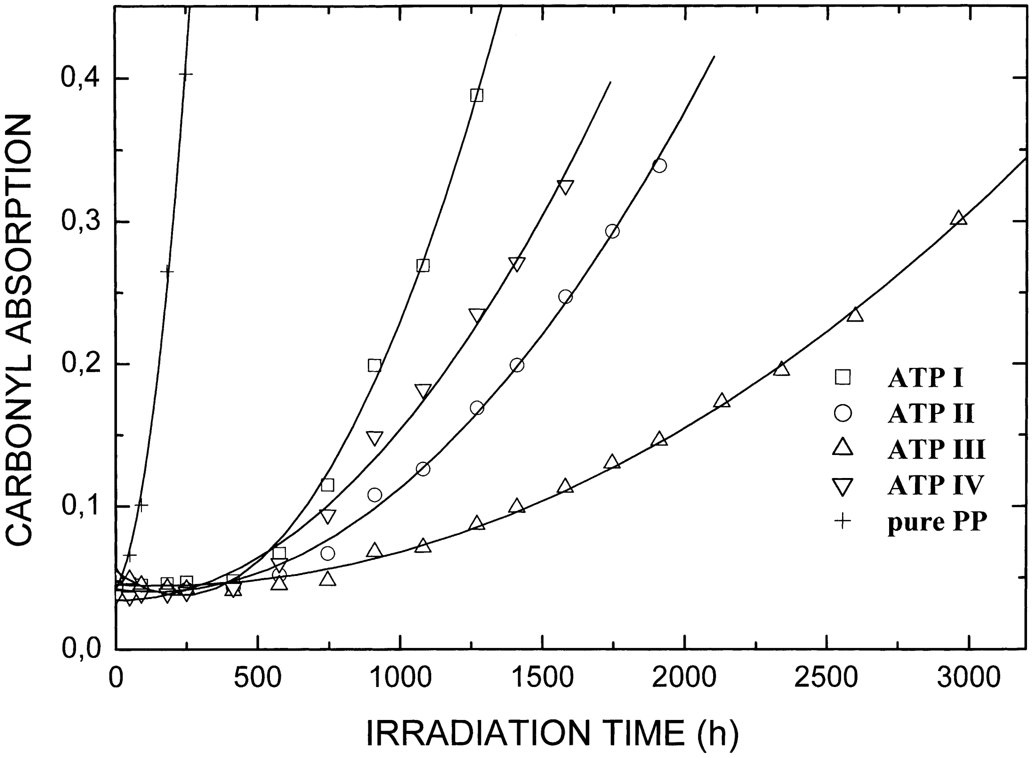


Fig. 1. Photo-oxidation of PP films (ca. 0.1 mm) prepared from partially oxidized PP powder containing combined derivatives of phenols **I–IV** and 4-amino-2,2,6,6-tetramethylpiperidine (**ATP**). Additives concentration 0.2 wt.%.

blended then processed in a Brabender Plastograph. In the case of photo-oxidation under the condition used non-stabilized PP film reached a carbonyl absorption of 0.2 after 170 h. This value is roughly equivalent to the loss of 50% of initial tensile strength. The stabilizing efficiency of combined phenol/HAS depends on the HAS as well as phenol structure. Concerning the HAS structure the best results have been reached with TMP derivatives for all phenols used—Fig. 3. Derivatives of BATP and ATP were less effective and their stabilizing effects were roughly similar—Figs. 1 and 2. Careful insight revealed that all derivatives of BATP are a little more efficient than the derivatives of ATP. This seems to be the effect of the *n*-butyl group in BATP. The presence of this not very long alkyl chain increased compatibility or solubility of these additives in non-polar PP matrix. The worst results were shown by PMP derivatives—Fig. 4. Usually the stabilizing efficiency of 2,2,6,6-tetramethyl and 1,2,2,6,6-pentamethylpiperidine derivatives of the same structure are very similar. In our case the difference between TMP and PMP derivatives is very pronounced. The biggest one is for the couple TMP III and PMP III. PP film containing TMP III reached carbonyl absorption 0.2 at 3 700 hrs while PMP III was at 1000 h. As will be shown later the big difference is not just in the case of combined phenol/HAS derivatives but there is similar difference between symmetrical TMP-TMP and PMP-PMP derivatives—Fig. 5.

The PP powder we used for the preparation of this set of films was partially oxidized. This can be seen from Figs. 1–7 where non-irradiated films revealed not very strong but definitely some carbonyl absorption. This value was ca. 0.06–0.08. This partially oxidized PP film is the reason for this big difference. As will be shown later this difference disappeared when fresh PP powder is used—Figs. 8 and 9. Most probably this difference is connected with the different efficiency of transformation of the parent amine to active form in the stabilization cycle—stable nitroxyl radical. The group $>NH$ in TMP derivatives is more easily converted to $>NO^{\bullet}$ compared with conversion of $>NCH_3$ in PMP derivatives. Conversion of parent amine TMP III and PMP III to the nitroxyl radical in the course of photo-oxidation is shown in Fig. 10. Fresh PP powder was used for preparation of these films. The conversion of PMP III to nitroxyl radical is much slower compared with TMP III conversion, especially in the first stage of irradiation. The concentration of $>NO^{\bullet}$ radical went through a maximum and than decreased to a stationary level. The same stationary level of $>NO^{\bullet}$ radicals was reached in the case of PMP III transformation in the later stage of irradiation. In the case of partially oxidized PP the

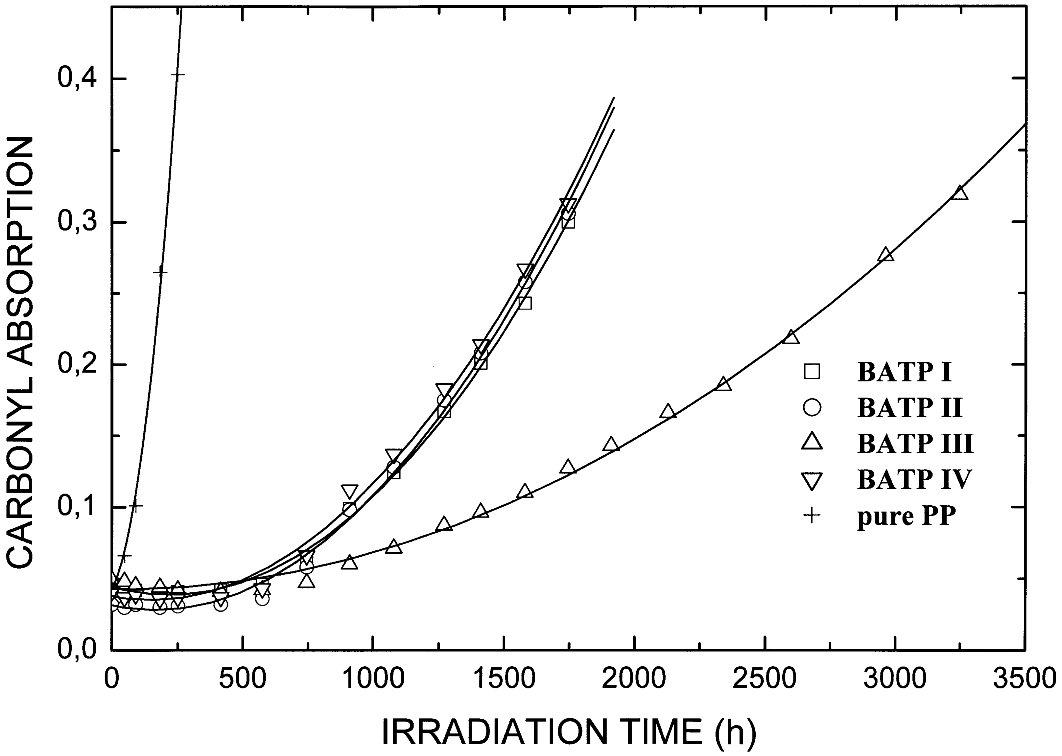


Fig. 2. Photo-oxidation of PP films (ca. 0.1 mm) prepared to be partially oxidized PP powder containing combined derivatives of phenols **I–IV** and 4-*N*-butyl-amino-2,2,6,6-tetramethylpiperidine (**BATP**). Additives concentration 0.2 wt.%.

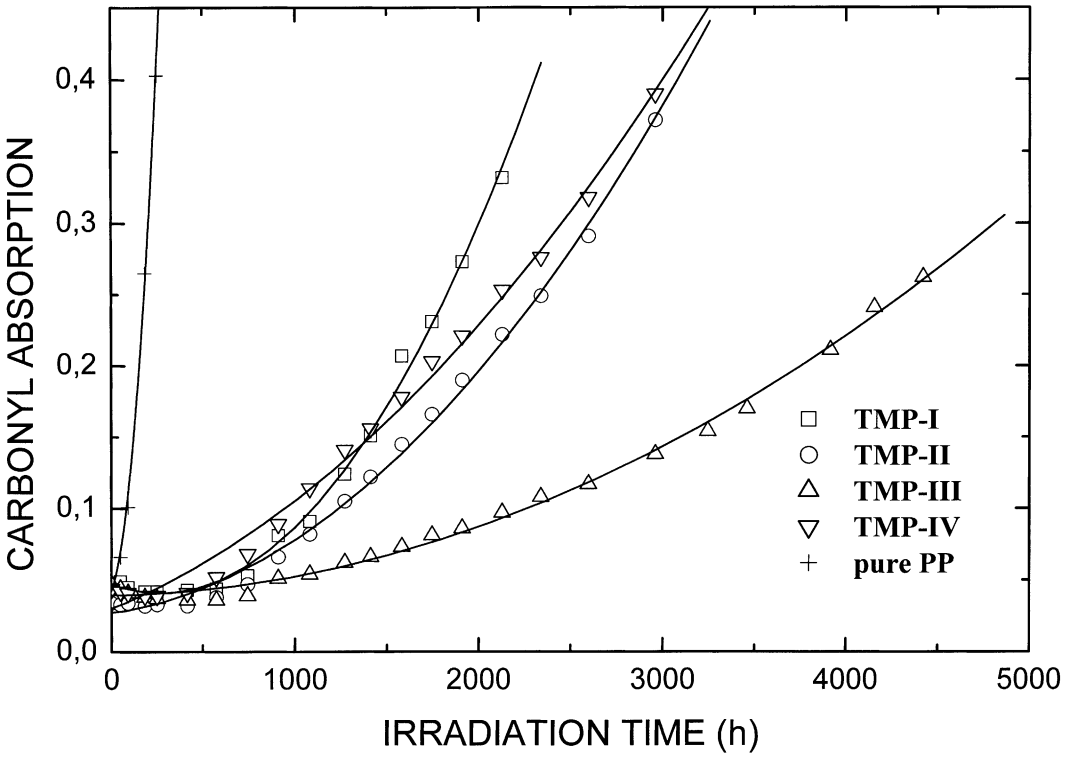


Fig. 3. Photo-oxidation of PP films (ca. 0.1 mm) prepared from partially oxidized PP powder containing combined derivatives of phenols **I–IV** and 4-hydroxy-2,2,6,6-tetramethylpiperidine (**TMP**). Additives concentration 0.2 wt.%.

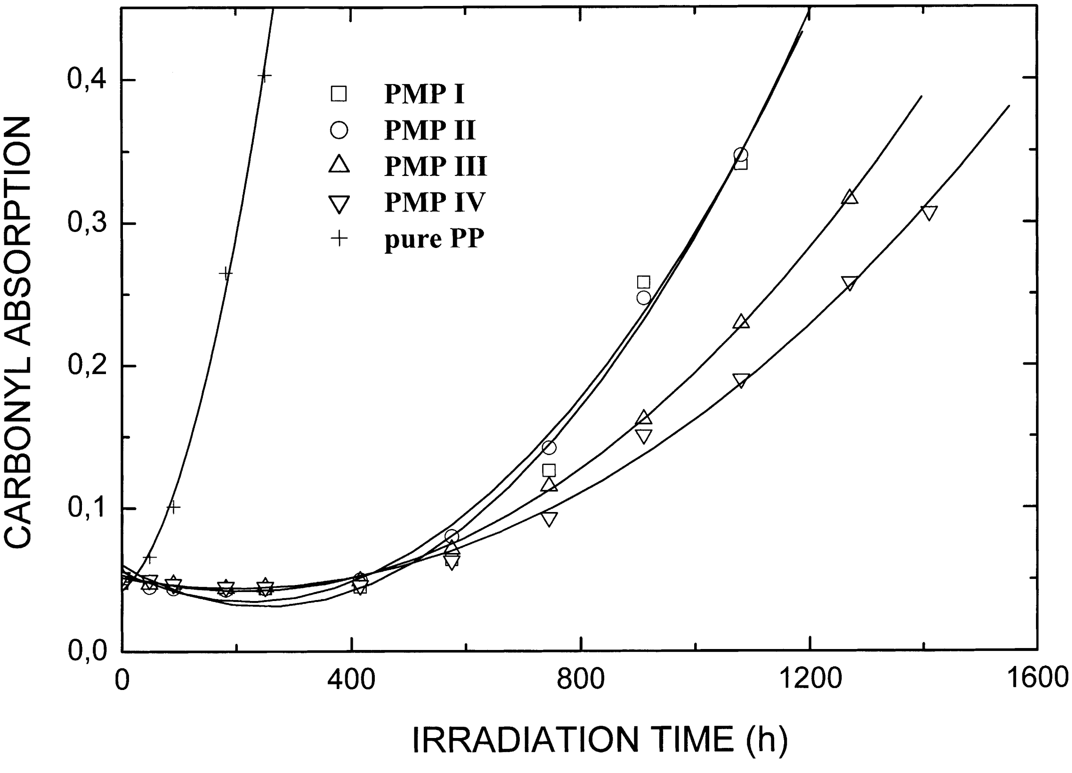


Fig. 4. Photo-oxidation of PP films (ca. 0.1 mm) prepared from partially oxidized PP powder containing combined derivatives of phenols **I–IV** and 4-hydroxy-1,2,2,6,6-pentamethyl-piperidine (**PMP**). Additives concentration 0.2 wt.%.

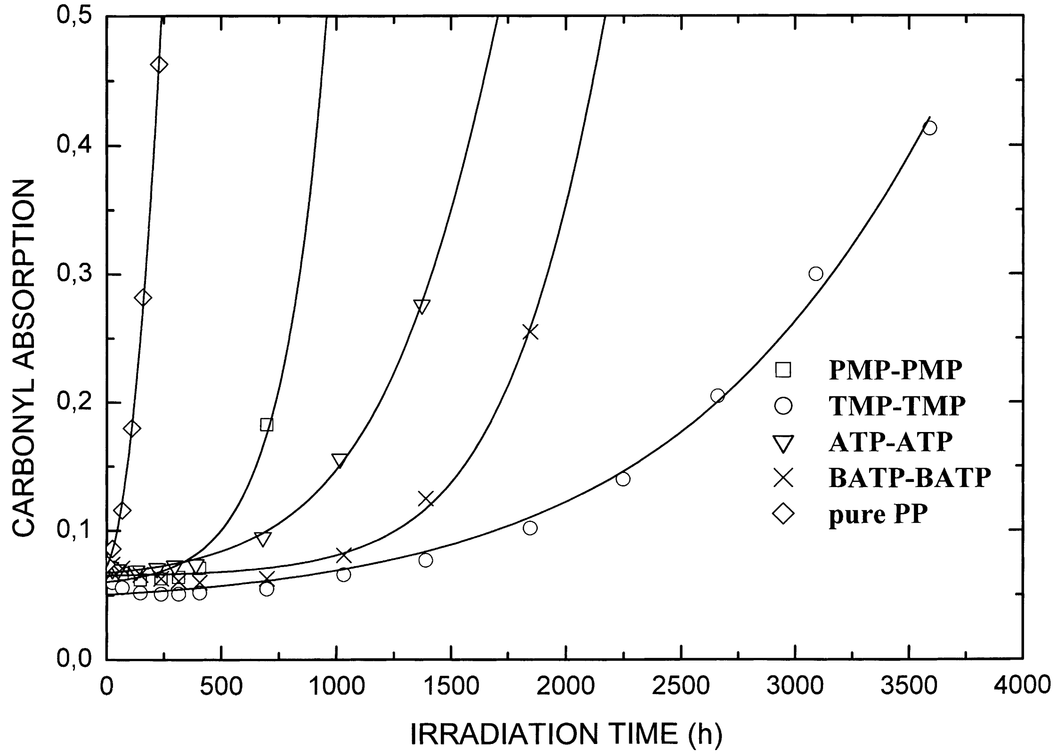


Fig. 5. Photo-oxidation of PP films (ca. 0.1 mm) prepared from partially oxidized PP powder containing symmetrical derivatives of HAS. Additives concentration 0.2 wt.%.

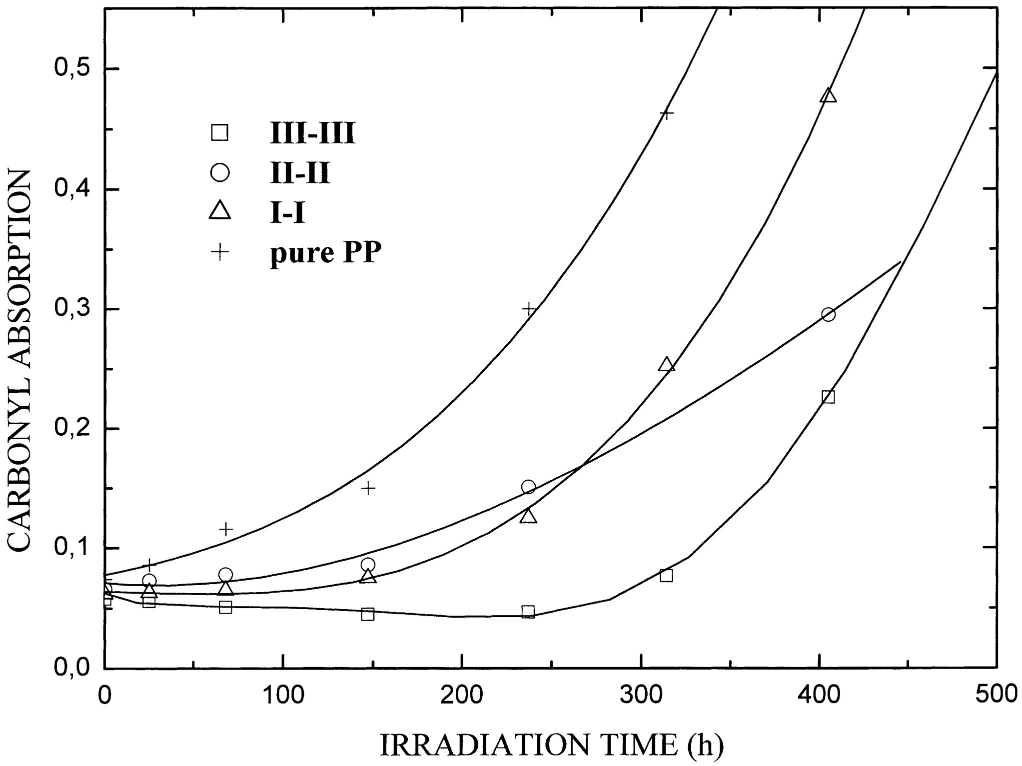


Fig. 6. Photo-oxidation of PP films (ca. 0.1 mm) prepared from partially oxidized PP powder containing symmetrical derivatives of phenols **I**, **II** and **III**. Additives concentration 0.2 wt.%.

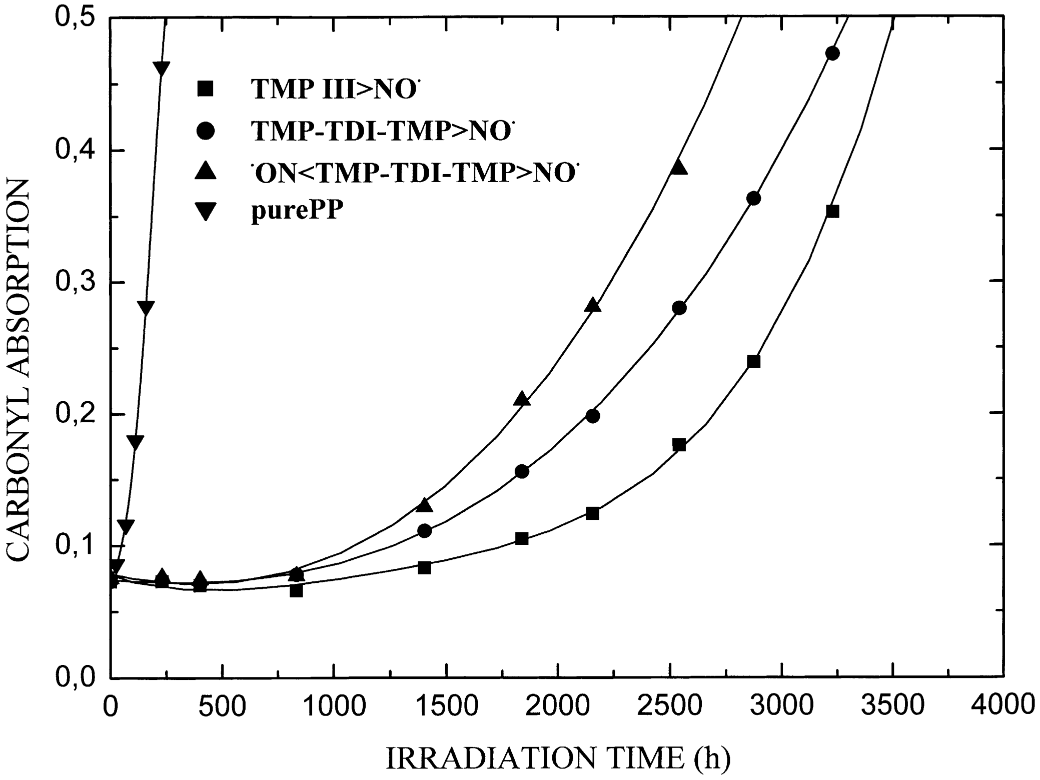


Fig. 7. Photo-oxidation of PP films (ca. 0.1 mm) prepared from partially oxidized PP powder containing combined and symmetrical derivatives of 4-hydroxy-2,2,6,6-tetramethylpiperidine in the form of stable nitroxyl radical. Additives concentration 0.2 wt.%.

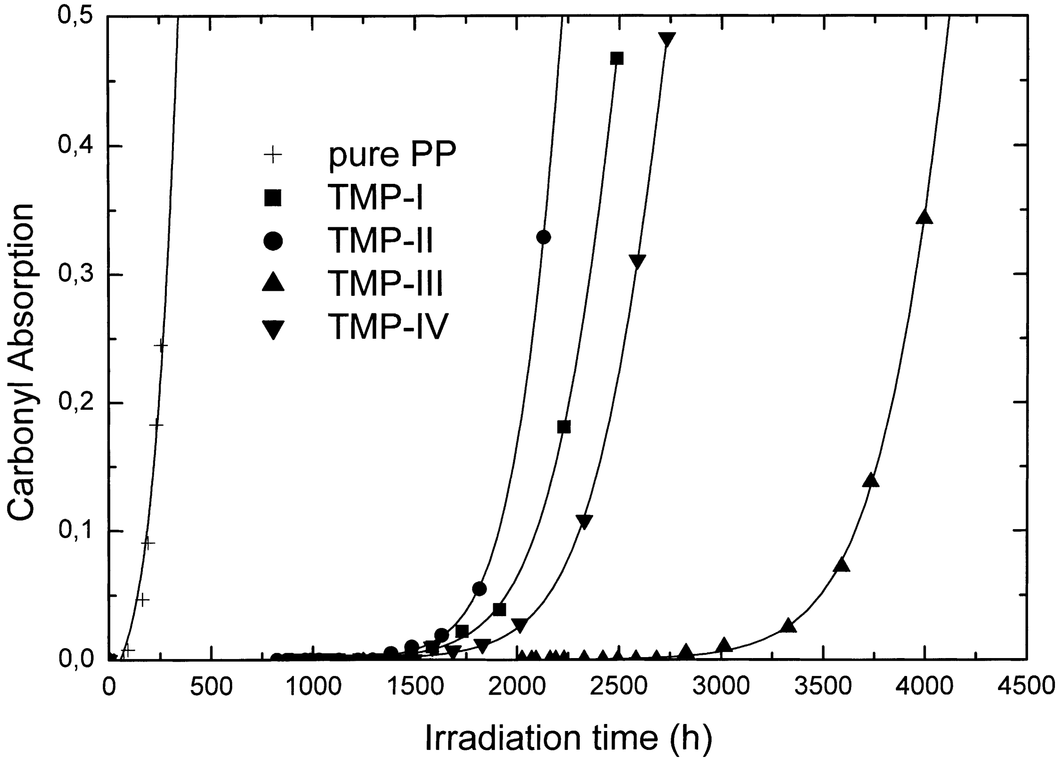


Fig. 8. Photo-oxidation of PP films (ca. 0.1 mm) prepared from non-oxidized (fresh) PP powder containing combined derivatives of phenols **I–IV** and 4-hydroxy-2,2,6,6-tetramethylpiperidine (**TMP**). Additives concentration 0.2 wt.%.

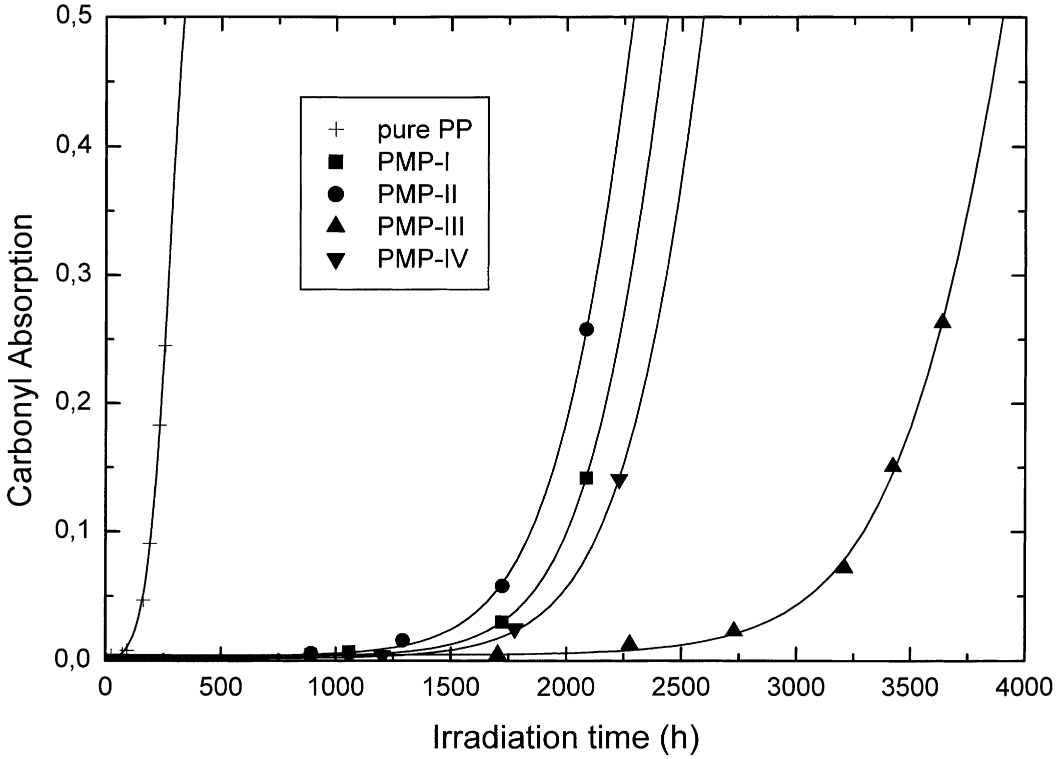


Fig. 9. Photo-oxidation of PP films (ca. 0.1 mm) prepared from non-oxidized (fresh) PP powder containing combined derivatives of phenols **I–IV** and 4-hydroxy-1,2,2,6,6-pentamethyl-piperidine (**PMP**). Additives concentration 0.2 wt.%.

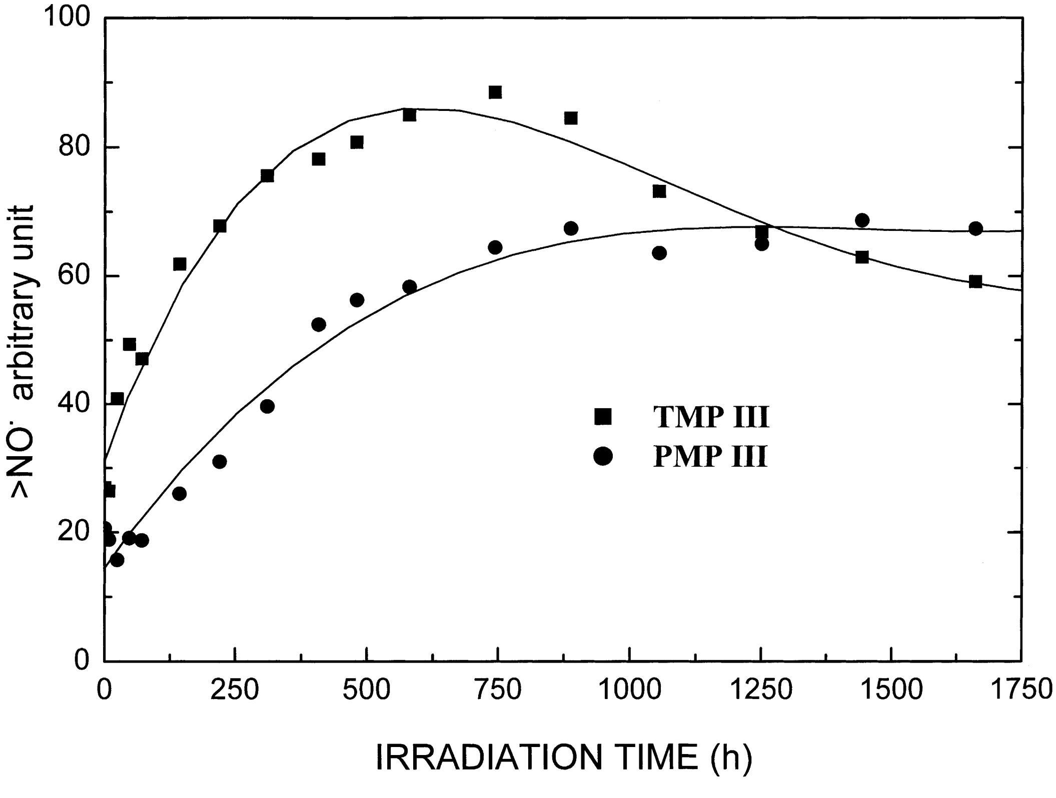


Fig. 10. Nitroxyl radical formation during photo oxidation of PP films (ca. 0.1 mm) prepared from non oxidized (fresh) PP powder containing combined derivatives of phenols **III** with 4-hydroxy-2,2,6,6-tetramethylpiperidine (**TMP**) and 4-hydroxy-1,2,2,6,6-pentamethyl-piperidine (**PMP**). Additive concentration 0.2 wt.%. Films were irradiated in ESR tubes.

slower rate of conversion of PMP III to $>NO^{\bullet}$ radical can be a crucial factor for the failure of stabilizing activity. Nitroxyl radicals formed in the later stage of photo oxidation are not able to stop or even compete with already started photo oxidation process activated by oxidation products present in the PP film before irradiation. This observation indicates that the efficiency of stabilizers of HAS type depends on the polymer to be stabilized as well. This means that PMP derivatives are not good candidates for stabilization of recycled polypropylene.

Concerning the effect of phenol structure on the stabilizing efficiency in the partially oxidized PP films the same order can be seen in the case of ATP and TMP derivatives—Figs. 1 and 3. The best efficiency was reached with 2,4-di-*tert*-butyl-6-methylphenol (**III**) followed by 2-*tert*-butyl-4-methylphenol (**II**) 2,4-di-*tert*-butyl-phenol (**IV**) and 2-*tert*-butyl-4-methoxyphenol. For BATP derivatives—Fig. 2—the best one was phenol **III** as in previous case followed by all three phenols with the same but lower activity. PMP derivatives behaved quite differently because of earlier mentioned reason. From Figs. 1–3 is clearly seen that the efficiency of the phenol III with substituents in both *ortho* positions is much better then for all phenols with only one substituent in *ortho* position

Fig. 5. shows the course of photo-oxidation of PP films containing symmetrical derivatives of HAS coupled through 2,4-toluenediisocyanate. The influence of HAS structure on the stabilizing efficiency is the same as it was in the case of combined phenol/HAS derivatives. The best efficiency was reached for the TMP–TMP product. The difference between stabilizing activity of BATP–BATP and ATP–ATP in this case is much bigger than it was in the case of comparison of combined BATP I–BATP IV and ATP I–ATP–IV (Figs. 1 and 2). In the symmetrical molecule the effect of the *n*-butyl chain is stressed by the presence of two HAS structural units in one molecule.

The most interesting conclusion comes from the comparison of the efficiency of combined phenol III/HAS i.e. ATP III, BATP III and TMP III and symmetrical HAS–HAS i.e. ATP–ATP, BATP–BATP and TMP–TMP. In the case of combined phenol/HAS ATP III the time to reach carbonyl absorption 0.2 was 2300 h (Fig. 1) while in the case of symmetrical HAS ATP–ATP (Fig. 5) this value is much lower at 1200 h. For derivatives of BATP it drops from 2500 h for BATP III (Fig. 2) to 1700 h for BATP–BATP and for TMP ones again fall from 3700 h for combined TMP III (Fig. 3) to 2700 h for symmetrical TMP–TMP. It is interesting to note that these differences are very similar. For the ATP derivatives it is 1100 h, for BATP ones 800 h and for compounds containing TMP it is 1000 h. The concentration of active HAS structural units is two times higher in symmetrical derivatives ATP–ATP, BATP–BATP and TMP–TMP compared with combined ATP III, BATP III and TMP III. The concentration of additives was 0.2 wt.% in all cases. So the half concentration of active HAS structural units in combined derivatives ATP III, BATP III and TMP III is able to protect polymer matrix about 1000 hrs longer then the double concentration of the same active HAS units in symmetrical ATP–ATP, BATP–BATP and TMP–TMP. This result points out on a quite strong synergistic effect of combination of phenol and HAS bonded through TDI. The contribution of the phenolic part itself is very small as can be seen from the courses of photo-oxidation of PP films containing symmetrical phenol I i.e. I-I, phenol II i.e. II-II and phenol III i.e. III-III (Fig. 6). Here again as in the case of combined phenol/HAS the efficiency of 2,6-di-substituted phenol (III-III) is higher then the efficiencies of phenols with one substituent in *ortho* position (I-I and II-II).

A similar synergistic effect for combined phenol/HAS but not so pronounced can be seen in Fig. 7 for TMP derivatives in the form of their stable nitroxyl radicals. Again the stabilizing efficiency of combined TMP III in form of nitroxyl radical–TMP III $>NO^{\bullet}$ is the best followed by the additive TMP–TMP $>NO^{\bullet}$ containing one HAS as a parent amine and one as a nitroxyl radical. The worst efficiency was found for the nitroxyl biradical $^{\bullet}ON<$TMP–TMP$>NO^{\bullet}$. The same conclusion can be done for the additives in form of nitroxyl radical as it was in the previous case for additives in the form of parent amines. Despite the half concentration of active part in TMP III $>NO^{\bullet}$ thanks to the synergistic effect of combination with phenol the stabilizing efficiency is better than in the case of using TMP–TMP $>NO^{\bullet}$ as well as $^{\bullet}ON<$TMP–TMP$>NO^{\bullet}$.

3.3. Photo-oxidation of fresh PP

Figs. 8 and 9 show the course of photo-oxidation of PP films prepared from fresh non-oxidized PP powder containing derivatives of 4-hydroxy-2,2,6,6-tetramethylpiperidine TMP I to TMP IV and 4-hydroxy-1,2,2,6,6-pentamethyl-piperidine PMP I to PMP IV. Comparison of results obtained from the photo-oxidation of partially oxidized PP films (Figs. 3 and 4) with results of the photo-oxidation of non-oxidized PP films points out the strong influence of HAS structure on the stabilizing activity. TMP derivatives are able to stabilize fresh non-oxidized PP as well as partially oxidized PP with roughly the same efficiency—compare Figs. 3 and 8. The best stabilizing effect is shown by TMP III in both cases followed by approximately the same but much lower protecting effect of derivatives TMP IV, TMP I and TMP II. This is the influence of phenol structure as has been already mentioned. There is just one difference between the courses of photo-oxidation of partially oxidized and non-oxidized PP samples.

Photo-oxidation of PP films prepared from partially oxidized PP powder recorded as a growth of carbonyl products absorption starts practically from the beginning of irradiation. Additives are not able completely to stop the already started oxidation and these two simultaneous processes resulted in smooth growth of the concentration of oxidation products from the start of irradiation. In the case of PP films prepared from non-oxidized PP powder an evident induction period can be seen. In this period no measurable amount of carbonyl oxidation products was detected. It means that in this case additives were able to inhibit all oxidation processes. After this period the photo-oxidation goes by very fast autocatalytic process. This difference in the behaviour of TMP derivatives is very small compared with the behaviour of PMP derivatives. The methyl substituent on nitrogen in PMP derivatives causing the different kinetics of conversion to stable nitroxyl radical was the reason for failure or pronounced decreasing of stabilizing efficiency in the case of photo-oxidation of PP films prepared from partially oxidized PP powder—Fig. 4. The change of PP matrix from partially oxidized to fresh non-oxidized resulted in completely different picture. Fig. 9 shows the courses of photo oxidation of PP films prepared from non-oxidized PP powder containing PMP derivatives. Stabilizing efficiencies increased to the values that are very similar with those of TMP derivatives.

To find the possible explanation for the synergistic effect of the combined phenol/HAS is very difficult. Actually we have the phenol in combined molecules in the form of carbamate. It does not possess a free –OH group that is essential for generally accepted the stabilizing mechanism of phenol. One possibility of the free phenol formation is during processing. The combined molecule may break down at the carbamate link releasing the free phenol. We measured the changes of UV spectra during photo-oxidation of PP films containing starting free phenol IV and additive TMP IV containing this phenol in combined molecule without a free –OH group. Free phenol IV in non-irradiated PP film showed two spectral bands at 275 and 220 nm—Fig. 11. Combined molecule TMP IV showed besides these two bands a shoulder at 250 nm—Fig. 12. This is absorption of 2,4-toluene coupling molecule. Comparison of absorbances at 275 and 220 nm showed that in the case of free phenol IV absorbance at 220 nm is half of that for the combined molecule TMP IV. So the much higher physical retention of the bigger combined molecules during processing in comparison with the retention of smaller parent free phenol can be one reason for better performance of combined molecules. Absorbance at 220

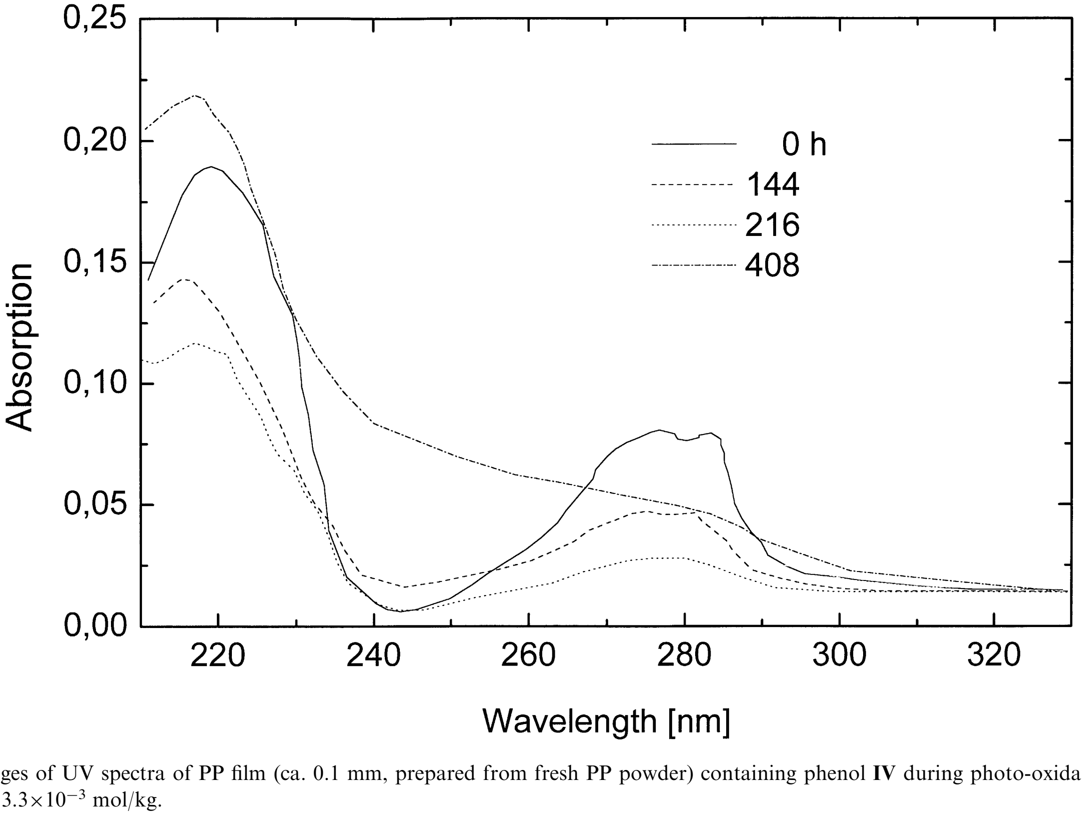


Fig. 11. Changes of UV spectra of PP film (ca. 0.1 mm, prepared from fresh PP powder) containing phenol **IV** during photo-oxidation. Additive concentration 3.3×10^{-3} mol/kg.

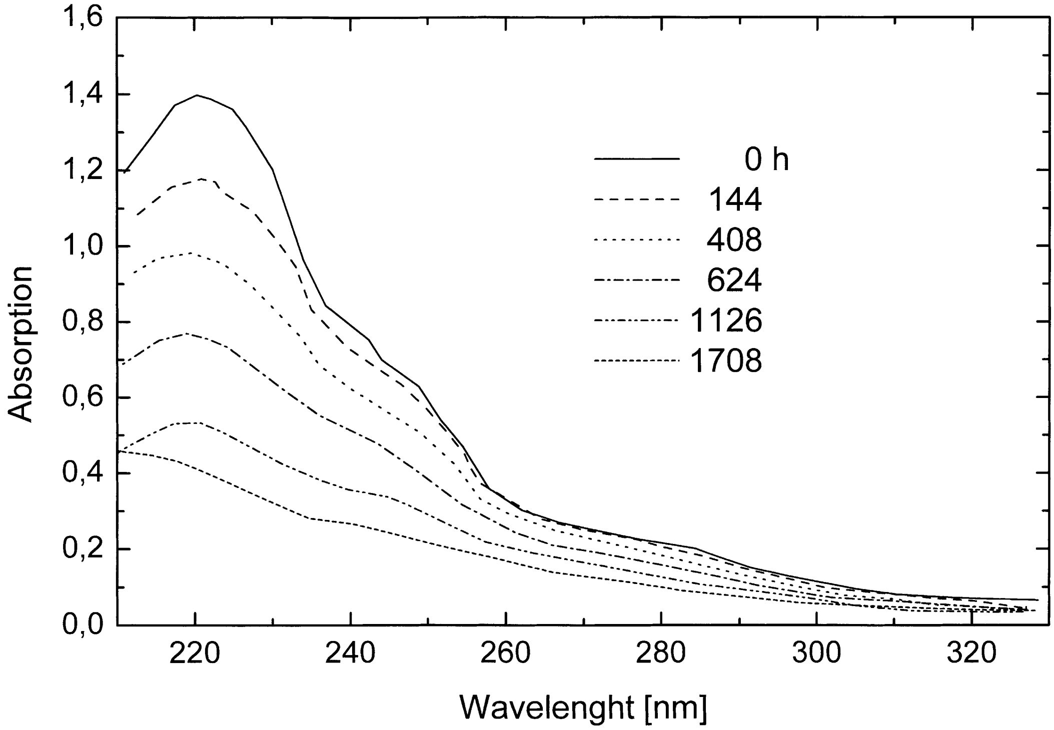


Fig. 12. Changes of UV spectra of PP film (ca. 0.1 mm, prepared from fresh PP powder) containing combine additive **TMP IV** during photo-oxidation. Additive concentration 0.2 wt.% = 3.3×10^{-3} mol/kg.

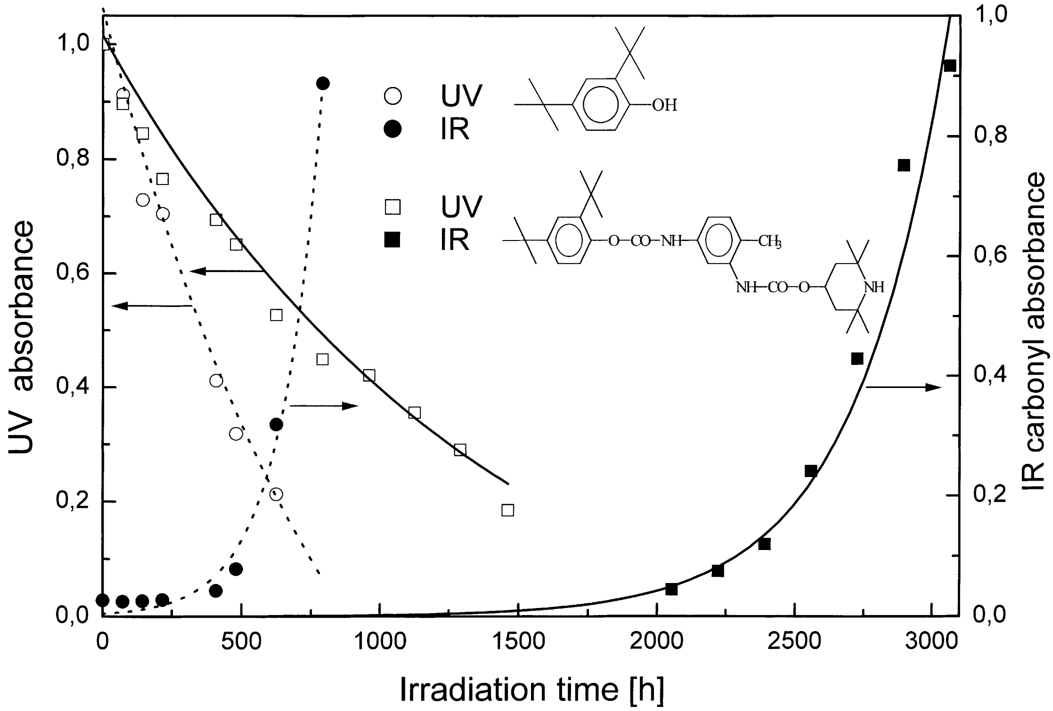


Fig. 13. Comparison of kinetics of additive consumption in PP film (ca. 0.1 mm, prepared from fresh PP powder) measured by UV spectroscopy for phenol IV and combined additive **TMP IV** and rates of photo-oxidation. Additive concentration 3.3×10^{-3} mol/kg.

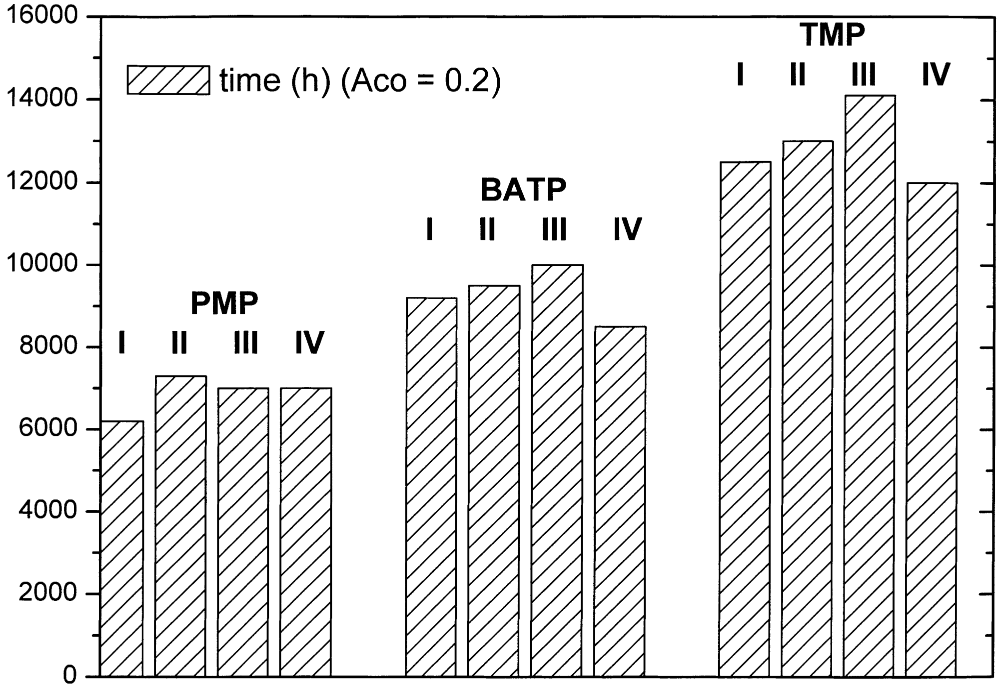


Fig. 14. Times to reach carbonyl absorption $A_{CO} = 0.2$ in thermal oxidation of PP films prepared from partially oxidized PP powder containing combined derivatives of **PMP**, **BATP** and **TMP**. Additives concentration 0.2 wt.%.

nm of the combined molecule TMP IV is about 7 times higher than for free phenol IV. So the combined molecule TPM IV has much higher UV protecting ability.

The kinetics of additives consumption during photo-oxidation are very different as well—Fig. 13. Free phenol IV is consumed much faster (decrease of absorption at 270 nm) in comparison with decrease of the same band in the case of combined TMP IV. (The repeated increase of absorption at 220 nm after ca. 400 h is because of production of absorbing species from oxidised PP. The same absorption band was seen for non-stabilised PP after ca. 100 h). Moreover, the photo-oxidation of PP film containing free phenol IV starts when there is still about 40% of phenol. The consumption of TMP IV is much slower possibly due to the protecting effect of HAS part of molecule. Due to the same effect the photo-oxidation of PP film containing TMP IV does not start at the point of 60% consumption as in the case of free phenol IV. The photo-oxidation starts after complete consumption of absorbing species. This means that the possible release of non-absorbing active HAS moieties is not working after consumption of absorbing groups from phenol and 2,4-toluene coupling. The decreasing UV absorptions is very smooth for all bands. This does not mean that combined molecules can not be broken down to smaller fragments.

3.4. Thermo-oxidation

Combined additives were also tested as a thermal stabilizers. PP film prepared from partially oxidized PP powder were used. Results for PMP, BATP and TMP derivatives are shown in Fig. 14. As in the case of photo-oxidation the worst results were found for PMP derivatives. But in this case it is questionable to evaluate these efficiencies as a failure. The time to reach carbonyl absorption 0.2 was very similar for all four PMP additives and represents values between 6000 and 7000 h. In comparison with the value of 24 h for non-stabilized PP film this is very good stabilizing activity. BATP derivatives reached this carbonyl absorption in period 8500 to 10,000 h. Influence of phenol structure on the efficiency is not so remarkable as in the case of photo-oxidation. Similar results as for BATP derivatives were obtained for ATP derivatives. The best thermo-stabilizing activity has been reached with TMP derivatives. The values between 12 000–14 000 represent really excellent thermal-stabilizing efficiency.

4. Conclusions

Preparation of coupled hindered phenols and HAS through the reaction with toluene 2,4-diisocyanate is a very convenient method for preparation of combined stabilizers with higher molecular mass. Reaction procedure as well as purification of products is very simple offering reasonable high yields. All combined phenol/HAS exhibited very good stabilizing efficiency in PP film prepared from non-oxidized PP powder. Their stabilizing activity depends on the structure of phenol as well as HAS. PMP derivatives are not good stabilizers for PP film prepared from partially oxidized PP powder. All other derivatives TMP, ATP and BATP are very efficient in both types of PP. Concerning the phenol structure the best efficiency was found for the 2,6-disubstituted phenol III. The efficiencies of phenols with just one substituent in the *ortho* position were much lower without unambiguous effect of different substituents in *para* position. Combined phenol/HAS stabilized PP much better than symmetrical HAS-HAS despite the half concentration of active HAS part in combined additives. The contribution of phenol part in photo-oxidation is very low. This was checked by testing symmetrical phenol-phenol. But its presence in combined derivatives increases the overall effect substantially. The reason for synergistic effect is not very well understood. The higher persistence (physical and photo-stability) might be the one reason. All combined derivatives of ATP, BATP, and PMP with all phenols used are good thermal stabilizers. TMP derivatives are the best with the time 12 000–14 000 h to reach carbonyl absorption 0.2.

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