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Dedicated to the 80th Birthday of Dr. Otto Vogl, Herman F. Mark Professor Emeritus

Photo-oxidation and Stabilization of sPP and iPP/Boehmite-Disperal Nanocomposites

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Photo-oxidation studies on polypropylene (PP)/organoclay nanocomposites were performed. Nanocomposites of isotactic (iPP) and syndiotactic (sPP) polypropylene were prepared by melt compounding. The nanofiller was Boehmite Disperal OS2–alumina hydrates (Al(OH)O) modified by C10–C13 alkylbenzene sulfonic acid. The nanofiller content was 1, 5, and 10 wt%. There is a clear pro-degradation effect of filler for both types of polypropylene used. The extent of this effect depends on the amount of filler and type of polypropylene used. In the case of sPP samples, the pro-degradation effect is proportional to the amount of filler in the whole concentration range of filler content used. In the case of iPP, there is a pro-degradation plateau at 5 wt% content of filler and higher concentration of filler (10 wt%) does not increase the rate and the course of photo-oxidation. Two long term stabilizers of HAS family were tested - commercial oligomeric stabilizer Chimassorb 944 (CHIM) and synthesized combined HAS/phenol (TMP). Stabilizing efficiency depends on the filler content. CHIM is able to stabilize just the nanocomposites with the lowest content (1 wt%) of filler. There is no stabilizing effect of this HAS in the case of the higher amount of nanofiller (5 and 10 wt%) in both types of polypropylene. By contrast, the combined HAS/phenol-TMP revealed some stabilizing efficiency over the whole range of filler content. The possible reasons for this difference are discussed. Interactions of filler with some HAS stabilizers were studied in cyclohexane as a model liquid for polypropylene by UV-spectroscopy. Interaction resulted in the fixing of additive on filler. Much stronger interaction has been obtained for oligomeric CHIM in comparison with low molecular HAS.

Keywords: polypropylene nanocomposites; photo-oxidation; stabilization; hindered amine stabilizers–HAS; stabilizer/filler interaction

1 Introduction

In the past decade, polymer nanocomposites have received considerable attention in fundamental research, as well as in industrial exploitation. One reason for this is that individual polymers, their mixtures or classical composites cannot fulfill demands made upon modern engineering materials. A montmorillonite reinforced polyamide nanocomposite prepared by Usuki (1, 2) was the first successful attempt. Polymer layered silicate nanocomposites can be prepared from relatively polar polymers such as polyamide, polycarbonate, poly(methyl methacrylate), polyethylene oxide and polystyrene (1–6), as well as from non polar polymers as polypropylene and polyethylene (7–9). These nanocomposites were prepared by different approaches. One procedure utilizes a solution method. Organo-modified clay and polymer are dissolved in organic solvent and after solvent evaporation intercalated nanocomposites can be formed. A more standard procedure is the melt method. The molten thermoplastic is mixed with nanofiller under conditions needed to optimize the interaction. Modified thermoplastics and different compatibilizers are used to increase this interaction. A third approach represents the *in situ* formation of nanocomposites during polymerization. Mülhaupt et al. demonstrated the advantage of ethene homo- and copolymerization in the presence of layered silicates in comparison with nanocomposites prepared by melt compounding (7).

Polypropylene (PP) is one of the most commonly used polymer matrix. This is due to the attractive combination of benefits like low cost, wide variety of application, low weight, and reasonably good mechanical properties. Problems in connection with its application in composite

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materials are poor adhesion and dispersion of polar filler due to the non-polarity of polymer matrix. The challenge in preparing PP nanocomposites is to disperse hydrophilic inorganic nanofillers in a hydrophobic polymer matrix. To increase the polarity, usually maleic anhydride is grafted on PP and this grafted polymer is used as a compatibilizer. Another way is modification of the filler. The cations situated between layers are exchanged by organic cations such as alkylammonium ions, resulting in lowering the surface energy of the clay and allowing the monomers or molten polymer to be intercalated between the clay platelets. Nanocomposites of polypropylene with enhanced properties have been prepared in order to improve their competitiveness for engineering plastics application.

Engineering plastics are often used in outdoor applications. Performance during application is a key feature of any such type of plastics. PP is quite sensitive to deterioration under the action of light and heat. For most applications, especially in an outdoor environment, it is necessary to use a stabilizing system. PP nanocomposites were found to be more degradable than pure PP under UV irradiation (10–13).

The aim of the present study is to determine the influence of modified Boehmite nanofiller on the photo-oxidation of isotactic polypropylene (iPP) as well as syndiotactic polypropylene (sPP). Stabilizing activity of derivatives of Hindered Amine Stabilizer (HAS) family as Chimassorb 944 and one combined HAS/phenol has also been evaluated. Possible interaction of stabilizers with filler was examined with cyclohexane as a model system using UV-spectroscopy.

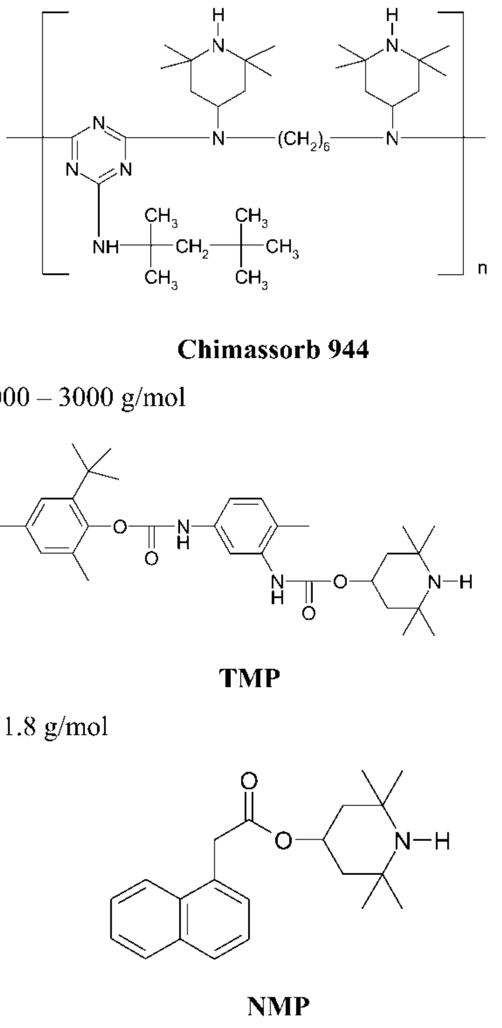
2 Experimental

2.1 Materials

The iPP used in these studies was a product of fy Borealis A/S, Denmark–type Borclean HC 101 BF with melt flow index (MFI) = 3.2 g/10 min at 230°C and melting point 161–165°C. It contains a processing stabilizing system, Irganox 1010 and Irgafos 168. The sPP component in the nanocomposite was a product of Total Fina, EOD 96-30, which had MFI of 4.4 g/10 min and melting point 130°C. The Boehmite nanofiller was Disperal OS2–alumina hydrates (Al(OH)O) modified by C10-C13 alkylbenzene sulfonic acid-from Sasol. Long term light and heat stabilizers of the HAS (Hindered Amine Stabilizer) family was oligomeric Chimassorb 944 (Ciba Specialty Chemicals), as well as the synthesized combined HAS/phenol compound-TMP. Synthesis and characterization of TMP is described in reference (14). The concentration of the stabilizer was 0.3 wt%. The structures of the stabilizers are shown in Scheme 1.

2.2 Preparation of Nanocomposite Samples

Preparation of the nanocomposite samples was done using a mini twin screw extruder (Werner & Pfleiderer, ZSK25).



Chimassorb 944

Molar mass: 2000 – 3000 g/mol

TMP

Molar mass: 551.8 g/mol

NMP

Molar mass: 325.4 g/mol

Sch. 1. Structures of long-term stabilizers.

The compounding was done at 190°C for 5 min at 100 rpm. Films were prepared in an electrically heated laboratory press (Fontune, The Netherlands) at 190°C for 1 min. The thickness of films was ca. 0.1 mm.

2.3 Photo-oxidation

Photo-oxidation was performed on a merry-go-round type setup. The irradiation source was a medium pressure 250 W mercury arc with a luminophore envelope (RVL, Tesla Holešovice, Czech Republic) with $\lambda > 310$ nm. The temperature of photo-oxidation was 30°C. The progress of chemical changes was followed by FTIR spectroscopy (NICOLET-400 Germany). The shape of the carbonyl band was broad, since it indicated the presence of several carbonyl products. The course of degradation is represented as the degree of carbonyl absorption (measured as the area of CO absorption bands divided by the film thickness) on the irradiation time.

2.4 Study of Filler-Stabilizer Interaction

A given amount of filler was dispersed in 0.3 wt% solution of stabilizer in cyclohexane. The dispersion was stirred for 20 h at room temperature. After centrifugation, the clear solution was diluted for UV measurements. Absorption spectra were taken on an UV-VIS Shimadzu 1650PC.

3 Results and Discussion

Photo-oxidation of iPP film leads to the formation of various carbonyl products (ketones, acids, esters, lactones) absorbing in the region of 1600–1850 cm^{-1}, as well as to different compounds with hydroxyl groups (hydroperoxides, alcohols) absorbing in the region of 3200–3600 cm^{-1} of the IR spectra. The changes in the carbonyl region of the FTIR spectra of pure iPP film, as well as iPP nanocomposite film containing 5 wt% of filler during photo-oxidation are shown in Figure 1. Naturally, the time-scale to reach similar carbonyl absorption for pure iPP (Figure 1a) is completely different as for the time-scale for iPP nanocomposite film (Figure 1b), but the shape of carbonyl envelope is very similar for both samples. Therefore, the composition of oxidation products is considered to be the same in both cases. This means that the mechanism of photo-oxidation of these iPP nanocomposites is the same as the known mechanism for pure iPP. The major difference is in the induction period of this process, which is much shorter for nanocomposites than for pure iPP. On the other hand, as will be seen later, the rate of photo-oxidation after the induction period is very similar for both cases. This indicates that the nanofiller (or some impurities in it, or modifiers) just initiates the process of photo-oxidation and thereafter the kinetics of the process proceeds as for pure iPP. The courses of degradation processes were followed by using carbonyl absorption changes in FTIR spectra. As mentioned earlier, the second region in the FTIR spectra useful for following the degradation process, is the region of hydroxyl absorption around 3200–3600 cm^{-1}. The reason we chose the carbonyl region is evident from Figure 2. Pure iPP film revealed a clear increase of OH-vibration with the time of irradiation (Figure 2a). However, these changes are not as evident in the case of the iPP nanocomposite film during irradiation (Figure 2b). One can see a shift in the spectra as a consequence of photo-oxidation and -OH group formation, but quantification of this process based on these shifts is definitely more questionable and less precise than for the carbonyl region. The reason for this difference in the IR spectra of -OH region between pure iPP and iPP nanocomposite is the presence of filler. The Boehmite alumina type nanofiller Disperal OS2 contains -OH groups. They are modified by the reaction with C10-C13-alkylbenzene sulphonic acid to decrease hydrophilicity and improve miscibility with non-polar, hydrophobic polymer matrix. This mixture contains -OH groups, which leads to -OH vibration in non-irradiated iPP nanocomposite films.

3.1 Photo-oxidation of iPP Nanocomposite Films

The courses of photo-oxidation of pure iPP and iPP nanocomposites containing different amount of filler are shown on Figure 3. Pure iPP is simply a film pressed from a given polymer matrix. This polymer contains a basic processing stabilizing system of Irganox 1010 and Irgafos 168. The stabilizers delay the onset of oxidation to ca. 400 h and carbonyl absorption reaches a value of 200 at 580 h. Under similar conditions of irradiation, usually for non-stabilized iPP, this value is found to be 200 h (14). Carbonyl absorption represents an integral value of the carbonyl envelope divided by film thickness. Carbonyl absorption of 200 in this scale corresponds roughly to 0.3 absorption at a maximum of carbonyl peak. There is a clear pro-degradation effect of filler. The presence of 1 wt% filler resulted in a decrease of time to reach the

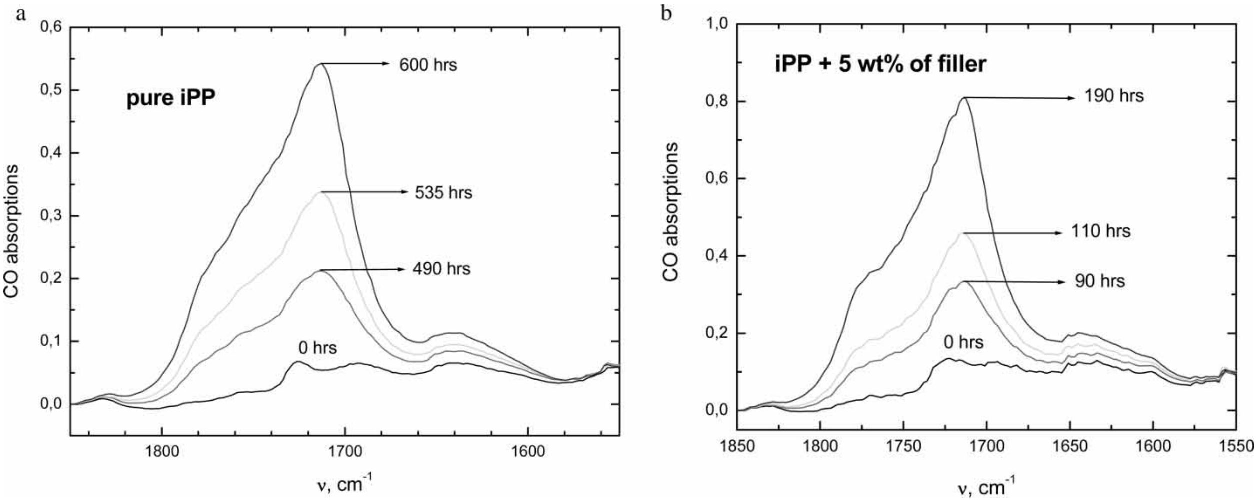


Fig. 1. Changes of the carbonyl region of FTIR spectra of pure iPP film (1a) and iPP nanocomposite film with 5 wt% of filler (1b) during photo-oxidation.

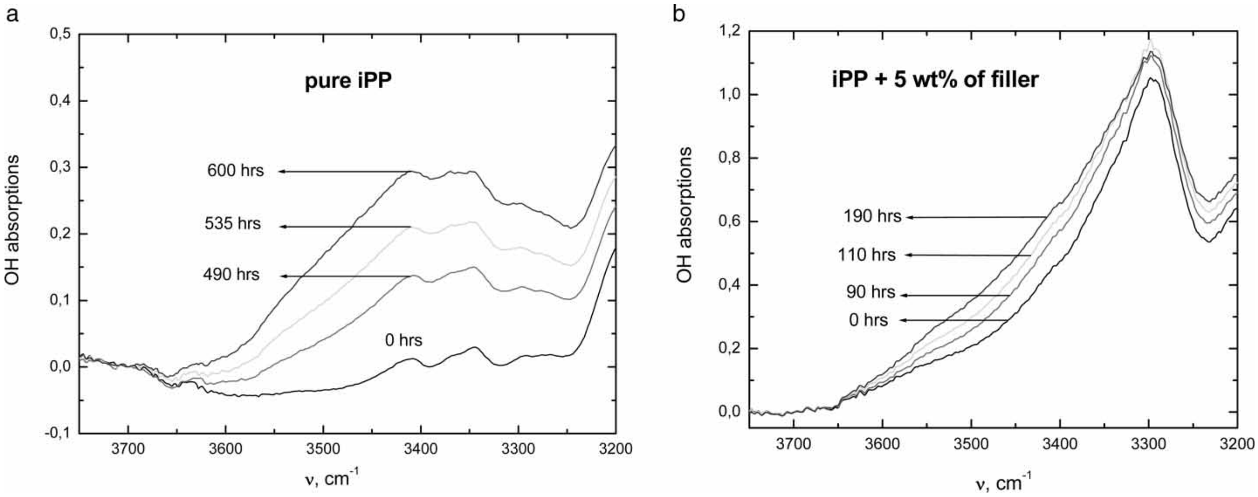


Fig. 2. Changes of the -OH vibrational region of FTIR spectra of pure iPP film (2a) and iPP nanocomposite film with 5 wt% of filler (2b) during photo-oxidation.

value of carbonyl absorption 200 from 580 h for pure iPP to 210 h for this nanocomposite film. At the higher filler content, the decrease is larger. For both samples containing 5 and 10 wt% of filler, this value is 120 h. This means that at the concentration of filler of 5 wt% (lower levels were not checked) there is a pro-degradation plateau and a higher concentration of filler (10 wt%) does not increase the rate and course of photo-oxidation. The presence of iron in the filler of a montmorillonite type and other silicates has been mentioned in the literature as one possible reason for pro-degradation (10). Iron in its ionic form can initiate the oxidation of polymers by a well-known redox reaction with hydroperoxides (15). Iron ions act principally as a catalyst for accelerated decomposition of hydroperoxides. This explanation can be just partially asserted for Disperal used in this study because it was prepared from very pure aluminum metal, and it is not a natural mineral product.

The course of the photo-oxidation of iPP nanocomposite films containing 0.3 wt% oligomeric HAS stabilizer CHIM are shown in Figure 4. In the case of the sample containing just 1 wt% of filler, effective stabilization of the nanocomposite film is observed. The difference in the time required to reach carbonyl absorption 200 for stabilized and non-stabilized sample containing 1 wt% of filler is 840 h (non-stabilized 210 h (Figure 3), stabilized 1150 h (Figure 4). This is quite a big improvement in comparison with values for samples having higher filler contents. Stabilized samples with 5 and 10 wt% of filler revealed much lower times to reach carbonyl absorption 200 in comparison with non-stabilized pure iPP, and there appears to be little dependence on the filler content. Despite the difference in improvement for the film containing a lower amount of filler (5 wt%) 80 h and higher amount (10 wt%) of filler 40 h, absolute values of improvement are almost negligible and the photo-

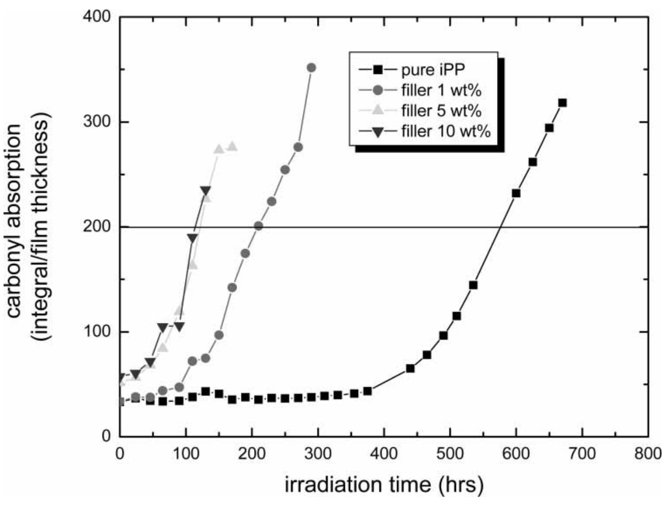


Fig. 3. Rates of photo-oxidation of nonstabilized iPP-nanocomposite films. Effect of increased nanofiller content.

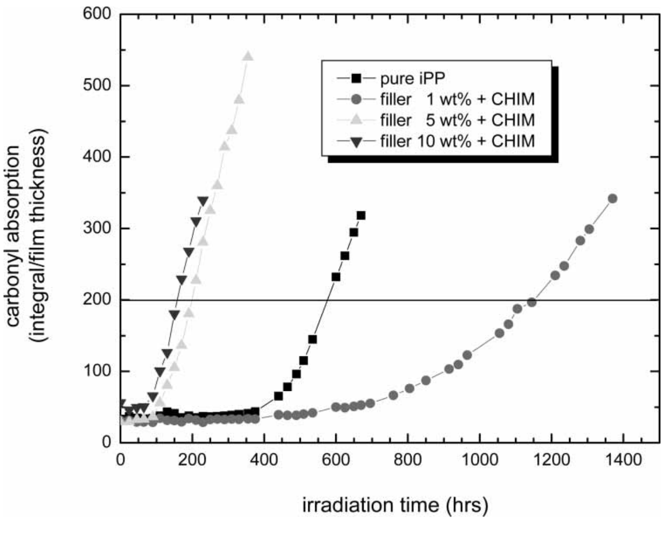


Fig. 4. Rates of photo-oxidation of iPP-nanocomposite films stabilized with Chimassorb 944. Stabilizer concentration 0.3 wt%.

oxidation proceeds roughly as with non-stabilized films (Figure 3). This means that in these two cases, the stabilizer is fixed on sites where it is almost completely inactive and is not able to take part in stabilizing action. Another interpretation is that photo-oxidation begins at locations where no stabilizer is present. Or, the stabilizer is in an inactive or much less efficient form. For example, in this particular case, as ammonium salt formed from a reaction of C10–C13 alkylbenzene sulfonic acid with very strong basic secondary amine group on the 2,2,6,6-tetramethylpiperidine ring. Stabilizing efficiency of HAS in the form of ammonium salt has been proved to be almost noneffective (16).

A different situation occurs in the case of combined stabilizer TMP. The courses of the photo-oxidation of iPP nanocomposite films containing 0.3 wt% of this combined HAS/phenol stabilizer are shown in Figure 5. One can see a clear influence of filler content on stabilizing efficiency of stabilizer for the entire range of concentrations. In comparison with CHIM, TMP is able to stabilize much better even those samples with a higher content of filler. As in the previous case, efficiency increases with decreasing the content of filler, but the absolute values are several times higher than for CHIM. For a sample with 10 wt% of filler, the increase is 180 h, for 5 wt% 370 h and for 1 wt%, it is 760 h to reach carbonyl absorption level 200 in comparison with non-stabilized films.

There is another explanation for lower efficiency in the case of CHIM when it is compared with TMP. CHIM is an oligomeric compound with molar mass 2000–3100 g/mol. Molar mass of TMP is 552 g/mol. Molar content of active 2,2,6,6-tetramethylpiperidine species is similar in both case, but the overall molar concentration of CHIM is five times lower (taking for calculation an average molar mass 2500 g/mol) than the molar concentration of TMP. Moreover, CHIM contains more sites for interaction with C10–C13 alkylbenzene sulfonic acid, and the probability of this reaction is much higher than in the case of TMP. Just one interaction in the case of CHIM is able to fix the whole oligomeric molecule containing several HAS active units at a place where it is not able to take part in stabilization action. In the case of TMP, such an interaction results in the deactivation of just one active unit. There are other groups in CHIM for this type of interaction. They represent one secondary and two tertiary amine groups present in the structure of this stabilizer. This reaction will also lead to a fixation of stabilizer on the filler.

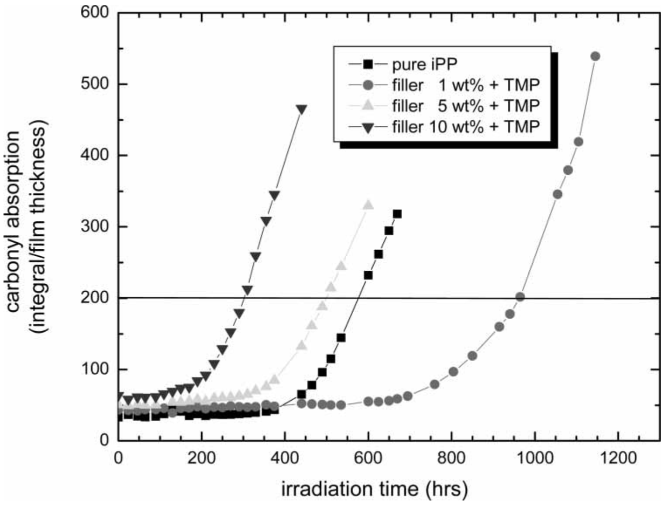


Fig. 5. Rates of photo-oxidation of iPP-nanocomposite films stabilized with combined HAS/phenol-TMP. Stabilizer concentration 0.3 wt%.

3.2 *Photo-oxidation of sPP Nanocomposite Films*

As in the case of iPP, a clear prodegradation effect of filler on the course of photo-oxidation of sPP can be seen in Figure 6. Contrary to the photo-oxidation of iPP nanocomposite films, in the case of sPP samples, the prodegradation effect is proportional to the amount of filler in the whole concentration range of used filler content. This relationship between filler content and time to reach carbonyl absorption 200 is not linear, but there is no plateau as in the case of iPP samples. This means that sPP polymer matrix is less sensitive to the prodegradation effect of this filler than is iPP matrix. This is reflected also in absolute values to reach the same carbonyl absorption 200. For iPP it is 120 h for 10 and 5 wt% of filler and 210 h for 1 wt% of filler (Figure 3) while for sPP it is 160 h, 200 h and 300 h for 10, 5 and 1 wt% of filler respectively (Figure 6).

The course of the photo-oxidation of sPP nanocomposite films containing 0.3 wt% of oligomeric HAS stabilizer CHIM are shown in Fig. 7. In the case of the sample containing just 1 wt% of filler, CHIM is able to stabilize the nanocomposite film. The interval of time needed to reach carbonyl absorption 200 is 500 h (non-stabilized 300 h (Figure 6), stabilized 800 h (Figure 7). Stabilized samples

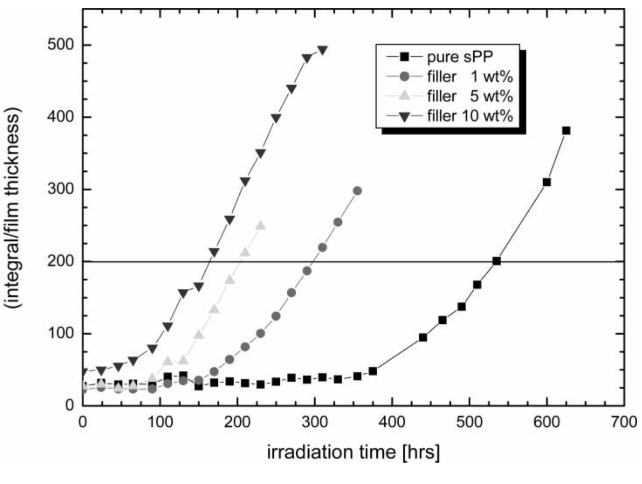


Fig. 6. Rates of photo-oxidation of sPP-nanocomposite films. Effect of increased nanofiller content.

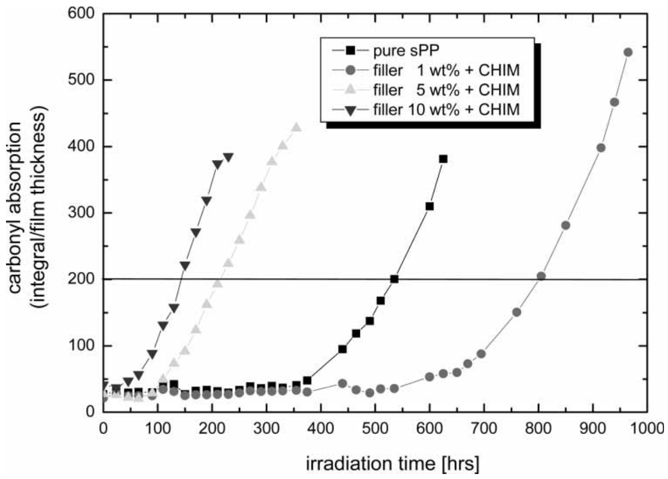


Fig. 7. Rates of photo-oxidation of sPP-nanocomposite films stabilized with Chimassorb 944. Stabilizer concentration 0.3 wt%.

with 5 and 10 wt% of filler degraded by the same rate and reached carbonyl absorption 200 at the same time as samples without stabilizer (Figure 6). This is the same behavior as observed in the case of iPP nanocomposite films containing CHIM and a higher amount of filler and the reasons are the same as has been already discussed for the family of iPP.

The stabilizing efficiences of combined HAS/phenol stabilizer, TMP, on the course of photo-oxidation of sPP nanocomposite films are shown in Figure 8. As in the case of the iPP nanocomposite (Figure 5), TMP contrary to CHIM, also revealed a stabilizing effect at higher filler contents (5 and 10 wt%). For the sample with 5 wt% of filler, there is an increase from 200 h for a non-stabilized sample to 430 h for a stabilized one to reach carbonyl absorption 200. For the sample with a filler content of 10 wt%, there is an increase from 160 h to 360 h.

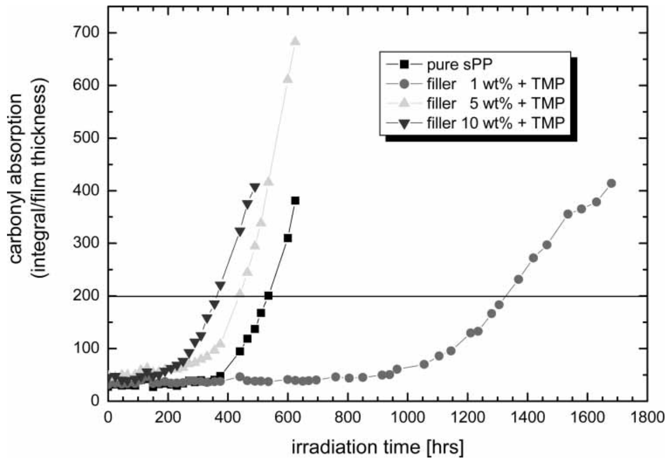


Fig. 8. Rates of photo-oxidation of sPP-nanocomposite films stabilized with combined HAS/phenol-TMP. Stabilizer concentration 0.3 wt%.

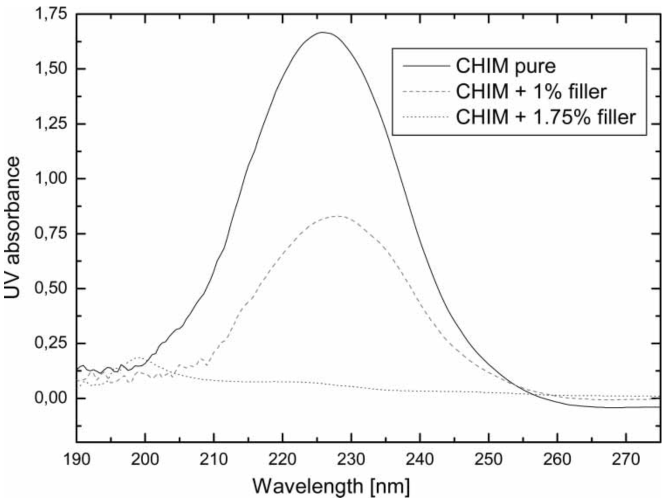


Fig. 9. Changes of UV-spectra of CHIM solution in cyclohexane resulting from interaction with filler.

3.3 *Filler–Stabilizer Interactions*

Possible interactions of filler with stabilizers were studied in cyclohexane as a model for polypropylene. Cyclohexane represents a non-polar solvent similar to non-polar PP. UV spectroscopy was used to evaluate the extent of interaction. The triazine ring in oligomeric CHIM is responsible for an absorption band with a maximum at 225 nm. Unfortunately, the second HAS stabilizer, TMP, at 0.3 wt% concentration, (as used for stabilization of PP) was not completely soluble in cyclohexane. Due to this, we chose NMP as a model for low molecular HAS. Moreover, this molecule contains a naphthyl ring, which has an absorption band at longer wavelength with maximum at 282 nm besides a short wavelength absorption band with a maximum at 225 nm. Using an absorption band around 220 nm was complicated by the fact that a small amount of C10-C13 alkylbenzene sulfonic acid was extracted from the filler into pure cyclohexane, and it absorbed in the same region with a maximum at 220 nm. Spectra were taken from transparent solutions after centrifugation to separate the filler, followed by proper dilution (100 ×). The amount of additive absorbed in the filler was calculated from the integral value (area under absorption band). Figure 9 shows the changes of UV spectra of oligomeric CHIM (0.3 wt%) due to the interaction

Table 1. Extent of fixing of additives on filler in cyclohexane solution

	Amount of additive in % absorbed on disperal from 0.3 wt% cyclohexane solution		
Additive	1 wt% DISP	1.75 wt% DISP	5 wt% DISP
CHIM	54	100	–
NMP	54	75	98

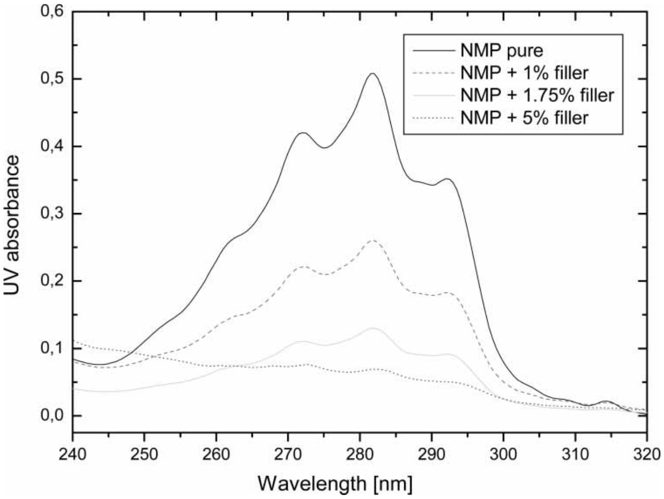


Fig. 10. Changes of UV-spectra of NMP solution in cyclohexane resulting from interaction with filler.

with Disperal in cyclohexane solutions. The lowest filler concentration used, 1 wt%, resulted in a very strong interaction with CHIM and less than half (46%, see Table 1) of the original amount stayed in the cyclohexane solution. Due to the fact that at 5 wt% filler content there was no absorption peak; we tested a lower concentration of filler. But even at 1.75 wt% concentration, there resulted an exhaustive fixation of CHIM on the filler. Different results were obtained in the case of low molecular NMP. The changes of UV spectra are shown in Figure 10 and the results of calculations on the basis of integral values are seen in Table 1. Analogous to CHIM, the lowest amount of filler, 1 wt%, resulted in the same extent of interception. But contrary to CHIM, the higher amount of filler, 1.75 wt%, did not fix all NMP, as in the case of CHIM. Still, 25% of the original amount remained in cyclohexane solution. Even at filler content of 5 wt%, there is some trace of NMP in cyclohexane solution. Quantitative results of the extent of the stabilizers – filler interaction in cyclohexane as a model for PP - corroborate the statement of lower efficiency of CHIM in comparison with TMP in polypropylene due to its stronger interaction with filler.

4 Conclusions

The photo-oxidative degradation of PP/Boehmite-Disperal nanocomposite films was followed by FTIR spectroscopy. The nanofiller–alumina hydrates modified by C10–C13 alkylbenzene sulfonic acid–decreases the induction period, as well as the time to reach a particular carbonyl absorption, in comparison with pure polypropylene. The extensiveness of this effect depends on the type of PP used and on the concentration of filler. In the case of sPP, a pro-degradation effect is proportional to the amount of the filler within the whole concentration range used. For iPP, there is a plateau at 5 wt% filler content. A higher concentration (10 wt%) does not decrease the induction period or the time to reach a particular carbonyl absorption. The shapes of carbonyl envelopes of FTIR spectra of pure PP (iPP and sPP) and its nanocomposites are very similar. Composition of oxidation products is the same in both cases. This means that the mechanism of photo-oxidation of these PP nanocomposites is the same as the known mechanism for pure PP. The nanofiller (or some impurities in it, or modifiers) initiate the process of photo-oxidation, but later, the kinetics of the process proceeds as for pure PP.

Two long-term stabilizers of HAS type–commercial oligomeric CHIM and combined phenol/HAS TMP were tested. CHIM is able to stabilize iPP, as well as sPP nanocomposites only at the lowest 1 wt% content of filler. Conversely, TMP was able to stabilize iPP, as well as sPP nanocomposites within the whole range used (1–10 wt%). Besides the increased prodegradation effect at higher filler concentration, interaction of stabilizer with the filler leads to markedly greater loss of stabilizing efficiency for oligomeric CHIM in comparison with TMP. This is likely due to the differences in molecular mass and structure. These differences are responsible for much stronger interaction of CHIM with filler and its complete fixing on the filler at concentration higher than 1 wt%. Differences in the interactions of oligomeric HAS-CHIM and low molecular mass HAS–NMP with nanofiller were checked and proved by UV-spectroscopy in cyclohexane solutions as a model for polypropylene.

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