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Photo-Oxidation of sPP/Organoclay Nanocomposites

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Photo-oxidation of syndiotactic polypropylene–sPP/organoclay nanocomposites was performed. Nanocomposites were prepared in situ by melt compounding of sPP, compatibilizer (iPP grafted with maleic anhydride–iPP-g-MAN) and organoclay filler ME C18 (modified with octadecyl ammonium chains in intergaleries of layered silicate, of which silicate layers (about 1 nm thin) were exfoliated). The influence of ME C18 nanoparticles alone (in content region 1 to 15 wt%) and together with compatibilizer iPP-g-MAN on the photostability of the sPP nanocomposite was studied. It was found that the silicate ME C18 nanoparticles alone catalyze the photooxidation and shorten the induction period of photo-oxidation to one fourth (at the content of 5 wt% of ME C18) in comparison with unfilled sPP) and the presence of compatibilizer supports the photo-oxidation of sPP nanocomposite. The ME C18 nanoparticles decrease the efficiency of UV stabilizers. The rate of photo-oxidation of sPP/clay nanocomposite after the induction period is significantly higher than unfilled sPP. The mechanism of photo-oxidation is discussed.

Keywords photo-oxidation, sPP, organoclay sPP nanocomposite

Introduction

Recently, the study of photo-oxidation processes of polypropylene materials has not attracted the attention of researchers, even though some questions concerning the oxidation mechanism remained unanswered (1–5). However, recent developments in synthesis, properties and future applications of polypropylene/layered silicate nanocomposites has revived an interest in observing the matrix behavior of this new type of composite material when subjected to the photo-oxidation process (6–8). There is not only academic, but also commercial interest in fully understanding the properties of this

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material, because polymer/clay nanocomposites display generally a variety of desirable properties, compared to both conventional composites and unfilled bulk polymers. These special properties include mechanical strength, flame retardancy and dimensional stability. Some of such characteristic improvements have already been found in iPP/clay and also sPP/clay nanocomposites (9–11) and still new positive results about the behavior of this kind of nanocomposites are expected. That is why as potential new materials, PP nanocomposites, necessitate investigation from the standpoint of photo-aging behavior.

In our study, we have focused our attention on the photo-aging of syndiotactic polypropylene (sPP)-organo-clay nanocomposites. These composites are prepared by the combining of sPP with a layered siliceous clay whose surface was made non-polar by treatment with long chain alkylammonium salts and utilizing iPP grafted maleic anhydride (iPP-g-MAN) as a compatibilizer. The influence of nano-filler alone, as well as compatibilizer, on the rate of photo-oxidation was observed. The study was completed with the observation of the effect of the filler on diminution of the photo stabilizing efficiency of a commercial stabilizer.

Experimental

Materials

Syndiotactic Polypropylene-sPP. The sPP component in the nanocomposite was a product of Total Fina, EOD 96–30 which had a melt flow index (MFI) of 4.4 g/10 min and melting point 130°C. The synthetic clay used as nano-filler was fluorohectorite, produced by Group Coop Chemical Co., Japan. This was obtained by heating talcum and Na₂SiF₆ together to produce SOMASIF ME100. This was subsequently treated with protonated octadecylamine (C18) as reported elsewhere in more detail (10).

Compatibilizer

The maleic anhydride-grafted iPP polymers (iPP-g-MAN) used as compatibilizers were a lower molecular weight Licomont AR 504 (MAN units content ~3.5 wt% and $M_n \sim 2900$ g/mol) and a higher molecular weight Hostaprim HC5 with 4.2 wt% MAN units and $M_w \sim 7500$ g/mole produced by Clariant GmbH.

Stabilizers

The stabilizer was a synergistic blend of Irganox 1010 and Irgafos 168 in the ratio 4:1, produced by Ciba Special Chemicals. The UV stabilizer was Chimasorb 944 (0.3 wt%), a product of Ciba Special Chemicals.

Preparation of Syndiotactic Polypropylene (sPP) Nanocomposite

The sPP product was obtained from Total Fina, labelled sPP, EOD 96–30. PP and organoclay were premixed in a tumbling mixer with 0.3 wt% stabilizer (Irganox 1010/Irganox 168). This mixture was also melt blended with 0 till 20 wt% iPP-g-MAN (Hostaprim HC5), maleic anhydride (MAN) content of 4.2 wt% in a co-rotating twin-screw extruder (Werner & Pfleiderer; ZSK25) at 190°C.

Preparation of Films of sPP Nanocomposite Samples for Photo-oxidation Studies

The bulk polymeric nanocomposites were pressed into c.a. 0.2 mm films in an electrically heated laboratory press (Fontune, Vlaardingen, The Netherlands) at 130°C under 40 kN pressure for 5 min.

Photo-oxidation of sPP Nanocomposite Film Sample

The photo-oxidation was performed on samples positioned on a carousel holder. The irradiation source was a medium pressure 250 W mercury arc with luminophore envelope (RVL, Tesla Holešovice, Czech Republic). The surrounding ambient air was used as the oxygen source. The temperature of photo-oxidation was 30°C, and the progress of the reaction was followed by FTIR spectroscopy (NICOLET-400 Germany), by monitoring the increase of carbonyl absorption between 1700 and 1780 cm⁻¹, caused by oxidation products. The shape of the carbonyl band was broad as it reflected the presence of several carbonyl products. The course of molecular degradation was represented by the increase of carbonyl absorption (measured as the area of CO absorption bands divided by the film thickness) against the irradiation time.

Results and Discussion

Photo-oxidation of sPP Nanocomposite Prepared without Compatibilizer

In the first series of experiments, the influence of the nano-filler alone (5, 10 and 20 wt%) on the rate of photo-oxidation of the sPP nanocomposite was compared to photo-oxidation of unfilled sPP films. The studies were performed using the apparatus.

It was found that the induction period of photo-oxidation of sPP nanocomposite containing 5 wt% of ME C18 (Fig. 1, curve 4) was shortened roughly four times in comparison with unfilled sPP film (Fig. 1, curve 1). With a further increase of nano-filler content to 10 and 20 wt%, the induction periods of photo-oxidations were longer in comparison to the 5 wt% sample. The difference between 5 and 10 wt% filled samples (Fig. 1, curves 4 and 3) was minimal, but all induction periods of photo-oxidation of sPP nanocomposites were shorter than for the unfilled sPP sample. The shortening of the induction period of photo-oxidation in the presence of ME C18 nano-filler can be ascribed to the catalytic effect of the silicate nanoparticles which, due to their large surface area and the presence of aluminum and/or iron in the crystalline lattice, results in an acceleration in the photo-oxidation of sPP matrix (6, 8). On the other hand, a filler content increase from 10 to 20 wt% leads to a noticeable prolongation of induction period of photo-oxidation. This phenomenon may be caused by the “screening effect” of the nano-filler. Exfoliated particles of nano-filler, although very thin, are relatively broad planar particles, which achieve several hundreds angstroms of length and which are dispersed in the whole volume of the sPP nanocomposite (as described in our previous paper (10)) can create considerable opacity toward the transmission of UV irradiation through the nanocomposite film. This screening effect of the nano-filler can partly reduce the photo-oxidation of the sPP matrix in the deeper layers of the film. This effect would be more pronounced for 10% and 20% samples, in comparison to sample containing less (5 wt%) nano-filler. Thus, an increase of filler from 5 to 10 wt% does not significantly influence the photo-oxidation of sPP nanocomposite, and, in fact, there is a small enhancement of induction period (Fig. 1). The non-proportional influence of the filler on the

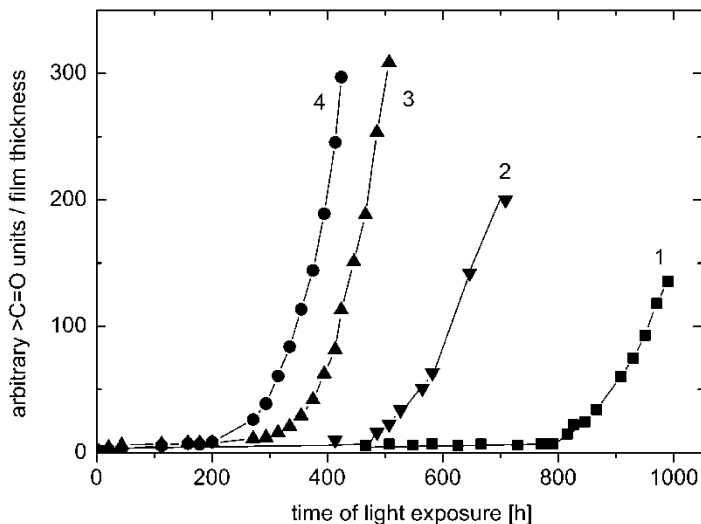


Figure 1. Time dependence of carbonyl groups formation during photo-oxidation of sPP/ME C18 nanocomposite (without compatibilizer). 1—pure sPP; 2—20 wt%; 3—10 wt%; 4—5 wt% of ME C18 filler.

screening effect can be caused by partial aggregation of filler. This phenomenon can be expected, because this series of nanocomposite samples does not contain any compatibilizer, which is needed from both the efficiency of exfoliation and uniform dispersion of the filler (10).

Photo-oxidation of sPP Organoclay Nanocomposite Containing Compatibilizer

A second series of sPP nanocomposite samples was prepared with the inclusion of a compatibilizer for the ME C18 filler. This compatibilizer is a maleic anhydride-grafted iPP (iPP - MAN) which is commercially available in two forms: one marked HC, containing higher molecular weight iPP and one marked AR, with lower molecular weight iPP. In the presence of compatibilizer HC, all samples of sPP nanocomposites gave a zero induction period on photo-oxidation (i.e., photo-oxidation started from the beginning of UV irradiation; Figs. 2 and 3). Also, a sample of sPP containing only the HC compatibilizer at 20% (Fig. 2, curve 4) shows a negligible induction period for photo-oxidation. Samples having ME C18 filler in the interval 5 to 10 wt% showed no difference in CO group production. This indicates that at these compositions of the sPP nanocomposites, the decisive role in formation of CO groups is determined by the amount of maleic anhydride groups linked to iPP chains, which are oxidized much more quickly than sPP alone.

The increased content of nano-filler, which from the previous results is considered as a catalyst of photo-oxidation, does not play any rôle, since there is practically no difference between oxidation curves of the sPP samples 5, 6 and 7 (Fig. 2). This can be explained by the concept that the photo-oxidation rate at such high content of compatibilizer is controlled by the rate of oxygen diffusion into the sample.

The fact that the compatibilizer plays an important role in photo-oxidation of sPP nanocomposite was revealed by the comparison of production of oxidation product containing carbonyl groups at different content of compatibilizer, 5, 10, and 20 wt%, and constant content of filler (5 wt%, Figure 2, curves 2, 3, 5). After 200 h

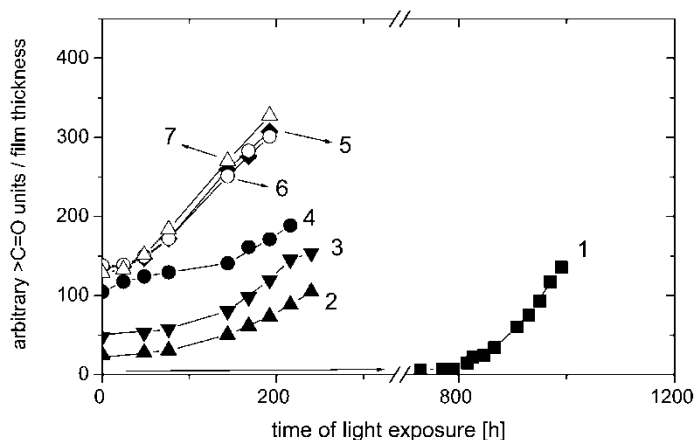


Figure 2. Time dependence of carbonyl groups formation during photo-oxidation of sPP/ME C18 nanocomposite at the presence of compatibilizer (of higher molecular weight-grafted iPP with maleic anhydride HC). 1—pure sPP; 2—sPP with 5 wt% ME C18 and 5 wt% HC; 3—sPP with 5 wt% ME C18 and 10 wt% HC; 4—sPP with 0 wt% ME C18 and 20 wt% HC; 5—sPP with 5 wt% ME C18 and 20 wt% HC; 6—sPP with 10 wt% ME C18 and 20 wt% HC; 7—sPP with 20 wt% ME C18 and 20 wt% HC.

of photo-oxidation of the above three samples, the relative production of CO groups, as determined by IR spectroscopy, was 50, 80 and ca 150 arbitrary units. The compatibilizer participated in activation of the photo-oxidation is confirmed by the determination that the presence of compatibilizer alone (without filler) in sPP shortens the inhibition

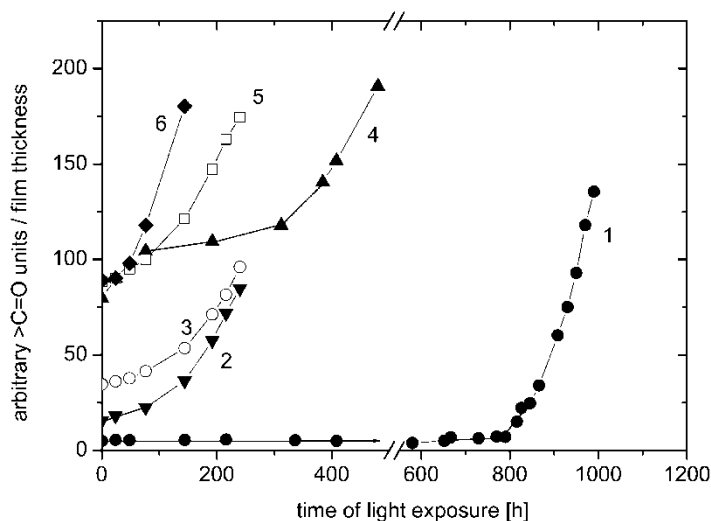


Figure 3. Time dependence of carbonyl groups formation during photo-oxidation of sPP/ME C18 nanocomposite at the presence of compatibilizer (of lower molecular weight-AR). 1—pure sPP; 2—sPP with 5 wt% ME C18 and 5 wt% AR; 3—sPP with 5 wt% ME C18 and 10 wt% AR; 4—sPP with 0 wt% ME C18 and 20 wt% AR; 5—sPP with 5 wt% ME C18 and 20 wt% AR; 6—sPP with 13 wt% ME C18 and 20 wt% AR.

period of photo-oxidation. This is indicated in Figure 2, curve 5 and more clearly in Figure 3, curve 4, in which the inhibition time is reduced from about 800 h to about 300 h.

At the same filler content (5 wt%), the compatibilizer with lower molecular weight, marked AR, influenced the photo-oxidation rate of sPP nanocomposite to a lesser degree than did the higher molecular weight compatibilizer HC. At compatibilizer content of 5 and 10 wt%, practically no difference in production, over time, of CO groups was found. However, at 20 wt% content of compatibilizer AR in the nanocomposite, the generation of CO groups was about 1/3 higher (Fig. 3, curves 2, 3, 5). Furthermore, an increase of filler content from 5 to 13 wt% gave a considerably enhanced photo-oxidation rate. The amount of CO groups generated was about 75 units greater even after just 100 h in comparison with photo-oxidation of sPP containing 5 wt% of filler (Fig. 3, curves 2 and 6).

With regard to the overall influence of both additive composite components in the sPP matrix, it can be stated that the presence of the nano-filler ME C18 alone results in an induction period of photo-oxidation (in our experiments in the interval 5 till 20 wt% of filler) that is considerably shortened by about one third. The large surface area of silicate particles, wherein aluminum atoms in the crystalline lattice are partially substituted by iron cations in the ratio $\text{Fe}/\text{Al} = 0.09$ (8) and the presence of octadecyl ammonium cations can be considered as responsible for photocatalytic activity in the nano-particles. Nanocomposite processing results in shortening of the induction period of photo-oxidation because of antioxidant consumption. The higher sensitivity of sPP nanocomposites, was similarly observed with iPP nanocomposites compounded with clay filler (6, 8).

The presence of compatibilizer in all sPP nanocomposite samples resulted in no observed induction period of photo-oxidation. Early in the first phase of photo-oxidation an enhancement of carbonyl groups was found. This enhancement early in the photo-oxidation process is most probably caused by the decomposition of anhydride groups in the compatibilizer (which was present at 5 to 20 wt% in the nanocomposite). Their free radical products initiate oxidation of the sPP matrix. With participation of the catalytic surface of nanoparticles, the result is a gradual formation of carbonyl groups, as has been described in the literature (6, 8). There is an interesting finding (8) that photo-oxidation of anhydride groups is not protected by the presence of antioxidants, even though they may protect sPP against photo-oxidation. The considerable shortening of induction period for photo-oxidation in the presence of a compatibilizer was observed also in a study of photo-oxidation of iPP silicate nanocomposite (8). The observation in our case that the induction period of photo-oxidation in the presence of compatibilizer was practically not observed (Figs. 2 and 3), leads us to assume that the surface of nanoparticles along with participation of the compatibilizer, are active also in thermo oxidation processes which take place during the preparation of sPP nanocomposite. In our case, the total amount of antioxidant present in the original polymer mixture was consumed. Therefore, UV irradiation of the samples and providing access to oxygen, resulted in immediate onset of the photo-oxidation process.

Influence of Nano-Filler on Efficiency of the Stabilizer

The influence of amount of nano-filler in the sPP nanocomposite was investigated relative to the stabilization efficiency of photo stabilizer toward photo-oxidation which was added at sPP nanocomposite preparation. An sPP nanocomposite containing

5 wt% ME C18 stabilized with 0.3 wt% UV stabilizer Chimasorb 944 and 0.3 wt% Irganox/Irgafos 168, showed an induction period for photo-oxidation that was prolonged from 200 (for unstabilized sample) to 600 h. Moreover, the rate of generation of CO groups after the induction period is much faster for unstabilized sPP nanocomposite sample. The increasing of oxidation products expressed in arbitrary units for time period 100 h was two times higher for unstabilized sample (170 a.u.) than for stabilized one (75 a.u.) (Fig. 4).

In the case of a sPP nanocomposite containing 10 wt% ME C18 and containing the same amount of stabilizer as in the previous sample, the induction period of photo-oxidation was prolonged only from 350 to 450 h (Fig. 5). The fact that the induction period of photo-oxidation of this unstabilized sample was longer than for the sample with 5 wt% of filler can be accounted for by the previously mentioned higher screening effect of the sample with 10 wt% of filler. On the other hand, a relatively small difference between stabilized and unstabilized samples indicates a considerable increase in the destruction rate of functional groups of stabilizer at the higher content of nano-filler ME C18 (Fig. 5). The rate of generation of CO groups during photo-oxidation of samples with 10 wt% ME C18 is a little higher (cca 200 arb. units/100 h) (Fig. 5) than in the case of the sample with 5 wt% ME C18 (cca 150 arb. units/100 h) (Fig. 4). These differences can be compared for samples containing 5; 7.5; and 10 wt% ME C18, which underwent photo-oxidation (Fig. 6). Thus, it is seen that in the case of stabilized samples of sPP nanocomposite, the order of shortening of induction periods is in agreement with the order of increasing filler content, although the differences are not excessive. The enhancement of photo-oxidation rate of sPP matrix after the induction period is proportional to the amount of filler. It appears that the screening effect of nano-filler, which was observed for photo-oxidation of unstabilized sPP nanocomposite samples (Fig. 1), does not influence remarkably the overall photo-oxidation rate. The screening effect of the filler did not reduce the photo-oxidation rate to such extent that at higher content of filler, longer induction periods were obtained than at lower content of filler. From this, it follows that the decrease of photo-oxidation effected by the

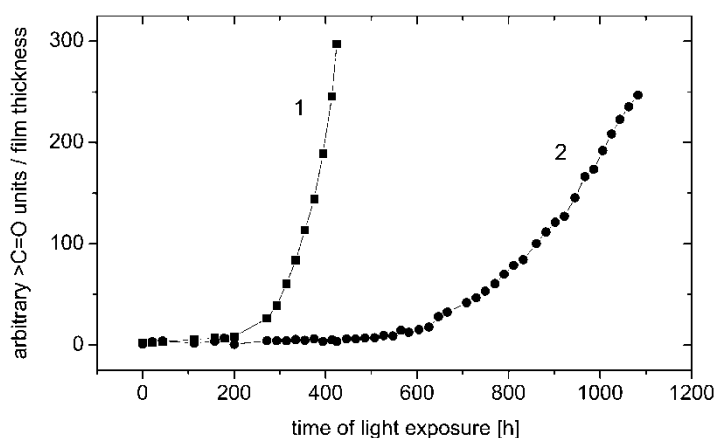


Figure 4. Comparison of photo-oxidation of stabilized and unstabilized sPP nanocomposite containing 5 wt% of ME C18 nano-filler. **1**—sPP with 5 wt% ME C18 without stabilizers; **2**—sPP with 5 wt% ME C18 and stabilized with 0.3% UV stabilizer Chimasorb 944 + 0.3% Irganox 1010/Irgafos 168 (4:1).

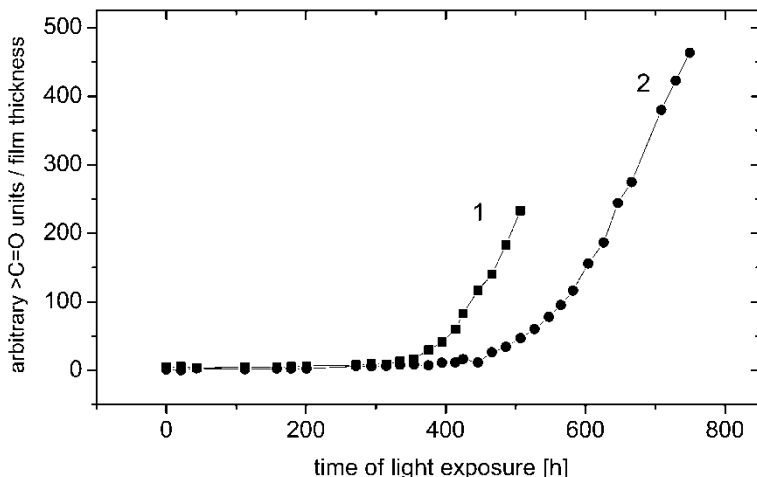


Figure 5. Comparison of photo-oxidation of stabilized and unstabilized sPP nanocomposites both containing 10 wt% of ME C18 nano-filler. **1**—sPP with 10 wt% ME C18 and without stabilizers; **2**—sPP with 10 wt% ME C18 and stabilized with 0.3% UV stabilizer Chimasorb 944 + 0.3% Irganox 1010/Irgafos 168 (4:1).

screening effect of higher amounts of filler located in deeper layers within the sample (more distant from the UV source) is offset by the higher photo-oxidation rate in the upper layers of the sample (closer to the UV source).

It is worth noting that the shape of carbonyl bonds envelope in the FTIR spectra is the same for all samples. Of course, the rate is completely different depending on the presence of filler and compatibilizer. It means that filler, as well as compatibilizer, change the kinetics of photo-oxidation, but the mechanism is the same for all samples.

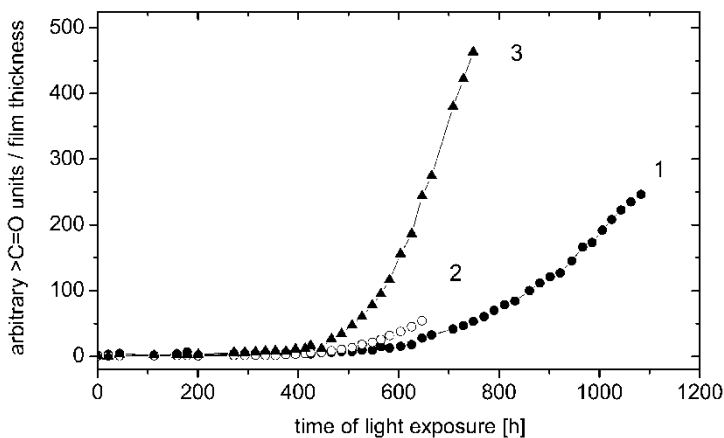


Figure 6. Comparison of photo-oxidation of stabilized sPP nanocomposite containing different wt% of ME C18 nano-filler: **1**—sPP with 5 wt% ME C18; **2**—sPP with 7.5 wt% ME C18; **3**—sPP with 10 wt% ME C18. All samples stabilized with 0.3% UV stabilizer Chimasorb 944 + 0.3% Irganox 1010/Irgafos 168 (4:1).

Conclusions

From this study of sPP/silicate clay nanocomposite photo-oxidation, the following conclusions are drawn:

The silicate clay nanoparticles catalyze the photo-oxidation process of sPP matrix.

The presence of iPP-g-MAN compatibilizer in sPP nanocomposite increases the rate of photo-oxidation.

Nano-particles of ME C18 significantly shorten the stabilizing effect of photo-stabilizer.

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