

# Natural photo-aging degradation of polypropylene nanocomposites

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## Abstract

The natural photo-aging degradation of polypropylene (PP), PP/CaCO<sub>3</sub> and PP/SiO<sub>2</sub> nanocomposites were studied outdoor for up to 88 days. The chemical structure characterized by Fourier transform infrared spectroscopy (FTIR) and pyrolysis gas chromatography–mass spectroscopy (PGC–MS) showed that PP nanocomposites are much more susceptible to photo-degradation than unfilled PP. And the oxidation rate is faster with more filler amount. There are lots of chain scissions happened in PP nanocomposites, accompanied with the formation of ketone, alcohol, ester and unsaturated double bond. This severe chain scission led to great decrease of  $M_n$  and  $M_w$ , and the consequent small fragments would re-crystallize and increase the crystallinity of the nanocomposites. However, these effects do not relate to the ultraviolet character of the two nano fillers.

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**Keywords:** Polypropylene; Nanocomposites; Photo-oxidation; Chain scission; Re-crystallization

## 1. Introduction

Since the successful development of montmorillonite reinforced polyamide nanocomposite by the Toyota group [1], polymer nanocomposites have received considerable attentions. Studies have shown that polymer nanocomposites exhibit remarkable properties, including high heat distortion temperatures, enhanced flame resistance, high modulus, perfect barrier properties and decreased thermal expansion coefficient, which may lead to applications in the automobile industry as well as the aircraft industry where materials with light weight but high heat-resistance are desirable.

The durability of polymer nanocomposites, as well as mechanical and thermal property, is also of great importance from the application point of view. Knowledge on aging behavior and mechanism of these materials is of great help for anti-aging research. Researchers studied photo-degradation behavior of different kinds of polymer/clay nanocomposites [2–5] and found opposite effect of clay on different polymer matrix. In polycarbonate (PC)/clay nanocomposites, clay helped to

improve PC's light stability [4], while in polyethylene (PE)/clay, polypropylene (PP)/clay and ethylene–propylene–diene monomer (EPDM)/clay nanocomposites, clay decreased these polymers' light stability [2,3,5]. However, the aging research is quite scarce compared to numerous reports on the modification of polymer nanocomposites. And limited works nearly all surround polymer/clay nanocomposites.

For PP nanocomposites, although in the past decades, researchers have done numerous work and obtained a good understanding about photo-degradation mechanism and photo-degradation products of PP [6–8], relatively few research reported on photo-aging of PP nanocomposites. Similarly, PP/clay nanocomposite occupied most of these reports. Mailhot et al. [5] studied the photo-chemical behavior of PP/clay nanocomposites. Tidjani and Wilkie [9] prepared PP/clay nanocomposites and studied their photo-oxidation stability. Qin et al. [10] investigated the photo-oxidation behavior of the PP/montmorillonite (MMT) nanocomposites upon ultraviolet exposure. They concluded that PP nanocomposites degraded much more rapidly than pure PP. The photo-oxidation of PP-based nanocomposites at wavelengths above 300 nm produced the same species and the same quantities of photoproducts as those of pure PP.

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Apart from clay, nano-CaCO<sub>3</sub> and SiO<sub>2</sub> are often used to improve the mechanical properties of PP as well. However, there is hardly any report on the outdoor durability of these nanocomposites. Leong et al. [11] studied the natural aging of conventional PP/CaCO<sub>3</sub> composite. Their result showed that the composite had a better retention in mechanical properties with some degree of surface degradation as well. Would the nano fillers have the similar effect as the conventional ones? In this work, the natural aging degradation of PP/CaCO<sub>3</sub> and PP/SiO<sub>2</sub> nanocomposites was carried out and the effects of these two nano fillers were evaluated.

## 2. Materials and experiments

### 2.1. Materials

Isotactic polypropylene F1002 (commercial grade, with melt flow index 1.7 g/10 min, from Yanshan Petrochemical Co. Ltd, Beijing, China) was used as received. Nano-CaCO<sub>3</sub>, 15 ± 5 nm in diameter, was supplied by Beijing University of Chemical Technology; nano-SiO<sub>2</sub>, about 40 nm in diameter, was supplied by Zhejiang Zhoushan Mingri Nanomaterial Co.

### 2.2. Nanocomposite preparation

The PP/CaCO<sub>3</sub> and PP/SiO<sub>2</sub> nanocomposites were prepared with a twin-screw extruder (TE-34 Jiangsu Keya Chemical Equipment Co. Ltd). The operating temperatures of the extruder zones were maintained at 200, 220, 220, 220, 220 and 210 °C from hopper to die, respectively. The screw speed was maintained at 50 r/min. After cooling in water, the extrudates were pelletized. The nanocomposites pellets were dried and then hot-pressed to films (about 120 μm in thickness) with pressure of about 10 MPa at 210 °C. The natural aging test was carried out outdoor for 88 days. After that, PP nanocomposite samples were broken into pieces. The compositions of the samples are listed in Table 1.

### 2.3. Characterizations

The Fourier transform infrared spectra were obtained using a Nicolet 560 FTIR spectrometer. Samples were analyzed by signal averaged from 32 scans at resolution of 4 cm<sup>-1</sup> in the wavenumber range of 4000–400 cm<sup>-1</sup>. It is used to monitor the variation of molecular structure of PP during weather

aging. In order to remove the influence of the sample thickness, peak at 2720 cm<sup>-1</sup> was used as reference [12].

The UV spectra of samples were collected by using a Shimadzu UV 2100S ultraviolet–visible spectrophotometer in the wavelength range of 200–800 nm.

The possible volatile molecules formed during the natural photo-oxidation in PP composites were analyzed with a pyrolysis gas chromatograph–mass spectrometer (PGC–MS) (SHIMADZU GCMS-QP5050A equipped with PYR 4A pyrolyzer). The flash evaporation technique was used to separate fragments due to chain scissions of PP molecules from the macromolecules. A sample was flash-heated at 300 °C for 30 s to evaporate only the fragments, while PP chain would not be broken at this temperature. The mixture of these products was carried through the fused silica capillary column (DB-5 25 m × 0.25 μm i.d.) by the carrier gas He and separated at the same time. Finally, each component was detected by the MS detector.

High temperature gel permeation chromatography (HGPC, Waters, Alliance GPCV2000, USA) was used for the characterization of molecular weights and molecular weight distributions of polypropylene fractions. The samples before and after light exposure were dissolved into 1,2,4-trichlorobenzene at 150 °C to make a very dilute solution with concentration of 0.1% by weight. Molecular weight was calculated based on the universal calibration curve of standard polystyrene.

The crystallinity of PP and its nanocomposites before and after exposure was determined by using a differential scanning calorimetry (DSC2910, TA Instruments). About 2.5 mg sample was heated from 50 to 200 °C at a rate of 10 °C/min under a nitrogen flow of 50 ml/min. The crystallinity was defined as follows:

$$X_c = \Delta H / (\Delta H_0 \rho) \quad (1)$$

where  $\Delta H$  was the measured melting enthalpy and  $\Delta H_0$  was the enthalpy of fusion of a 100% crystalline polypropylene ( $\Delta H_0 = 209 \text{ J/g}$  [13,14]);  $\rho$  was the content of polypropylene in matrix.

## 3. Results and discussion

Fig. 1 shows the IR spectra of PP and PP nanocomposites at different aging times. Since PP-C-3 and PP-S-3 broke into pieces after 88 days of exposure, comparison after longer exposure was not carried out. A new broad band appeared at about 1715 cm<sup>-1</sup> after exposure, which belongs to a mixture of different carbonyl species [5]. The second new band at about 3400 cm<sup>-1</sup> belongs to hydroxyl group, which indicates the generation of hydroperoxide and hydroxyl species. In addition, the intensity of the carbonyl and hydroxyl bands grew with increasing exposure time. The increasing rate of these bands of pure PP was lower than those of PP nanocomposites. For pure PP, the obvious oxidation occurred after 80 days, and developed slowly. For PP-C-3, although obvious oxidation was observed after 80 days, the band at 1711 cm<sup>-1</sup> increased sharply. For PP-S-3, oxidation evidence could be seen

Table 1  
Composition of PP nanocomposites

Sample number	Composition
PP-C-1	PP/CaCO <sub>3</sub> = 100/1
PP-C-3	PP/CaCO <sub>3</sub> = 100/3
PP-C-5	PP/CaCO <sub>3</sub> = 100/5
PP-S-2	PP/SiO <sub>2</sub> = 100/2
PP-S-3	PP/SiO <sub>2</sub> = 100/3
PP	PP

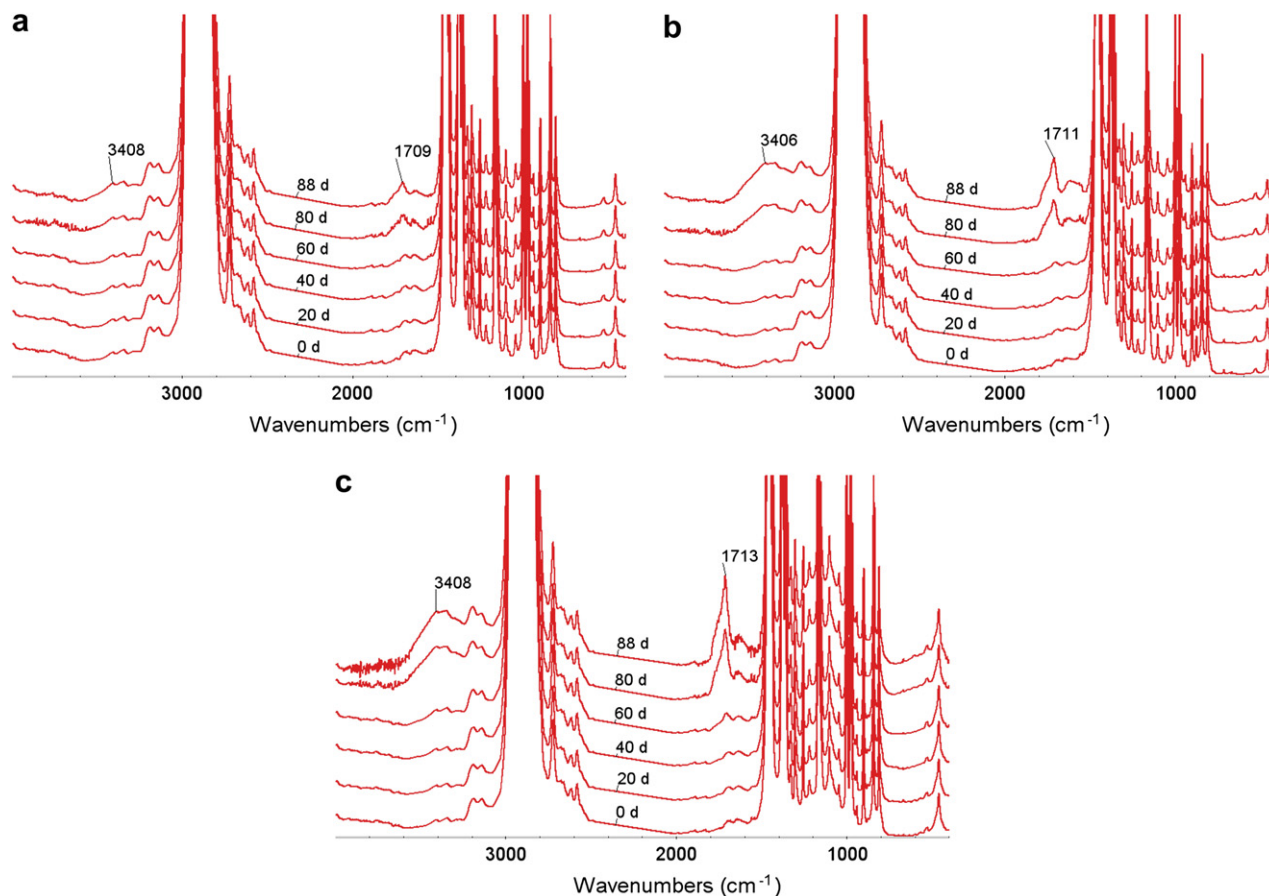


Fig. 1. The IR spectra of (a) PP, (b) PP/CaCO<sub>3</sub> and (c) PP/SiO<sub>2</sub> nanocomposites at different aging times.

after 60 days, and had a steep increase after 80 days. The IR spectra showed that the oxidation of PP nanocomposites is much more significant than that of pure PP, and the addition of nano fillers accelerated the oxidation of the matrix, like the role of clay in PP [1,5,9]. Because of the similar spectrum of PP and PP nanocomposites after 88 days of exposure, the pure PP and PP nanocomposites might have the same photo-degradation mechanism.

The effect of the concentration of the nano fillers on the photo-oxidation is shown in Figs. 2 and 3, from which one

can observe that the carbonyl and hydroxyl groups increased with the filler amount. The corrected absorbance of aged PP was only 0.58, while those of PP/CaCO<sub>3</sub> nanocomposites were 1.47, 2.00 and 3.48, with filler amount of 1, 3 and 5 wt%, respectively; those of PP/SiO<sub>2</sub> nanocomposites were 1.52 and 2.67, with filler amount of 2 and 3 wt%, respectively. Meanwhile, PP/SiO<sub>2</sub> had a higher oxidation degree than PP/CaCO<sub>3</sub> with the same filler content. The corrected absorbances of aged PP-S-3 and PP-C-3 were 2.67 and 2.00, respectively. For all the samples, there existed an induction period of

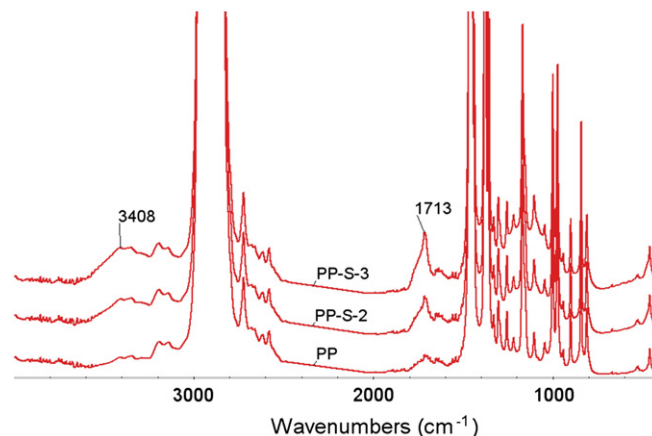
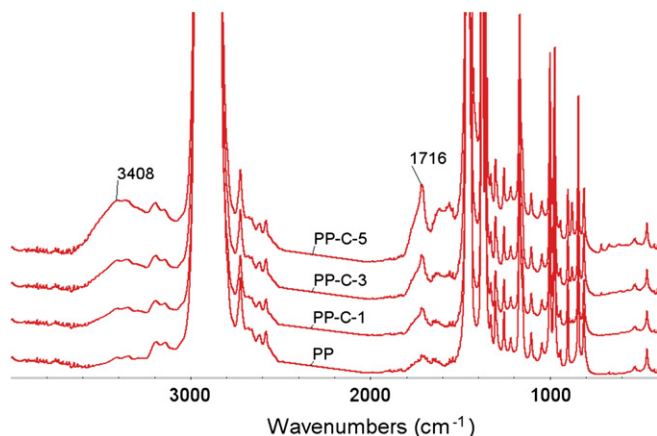


Fig. 2. The IR spectra of PP and PP/CaCO<sub>3</sub> nanocomposites after exposure.

Fig. 3. The IR spectra of PP and PP/SiO<sub>2</sub> nanocomposites after exposure.

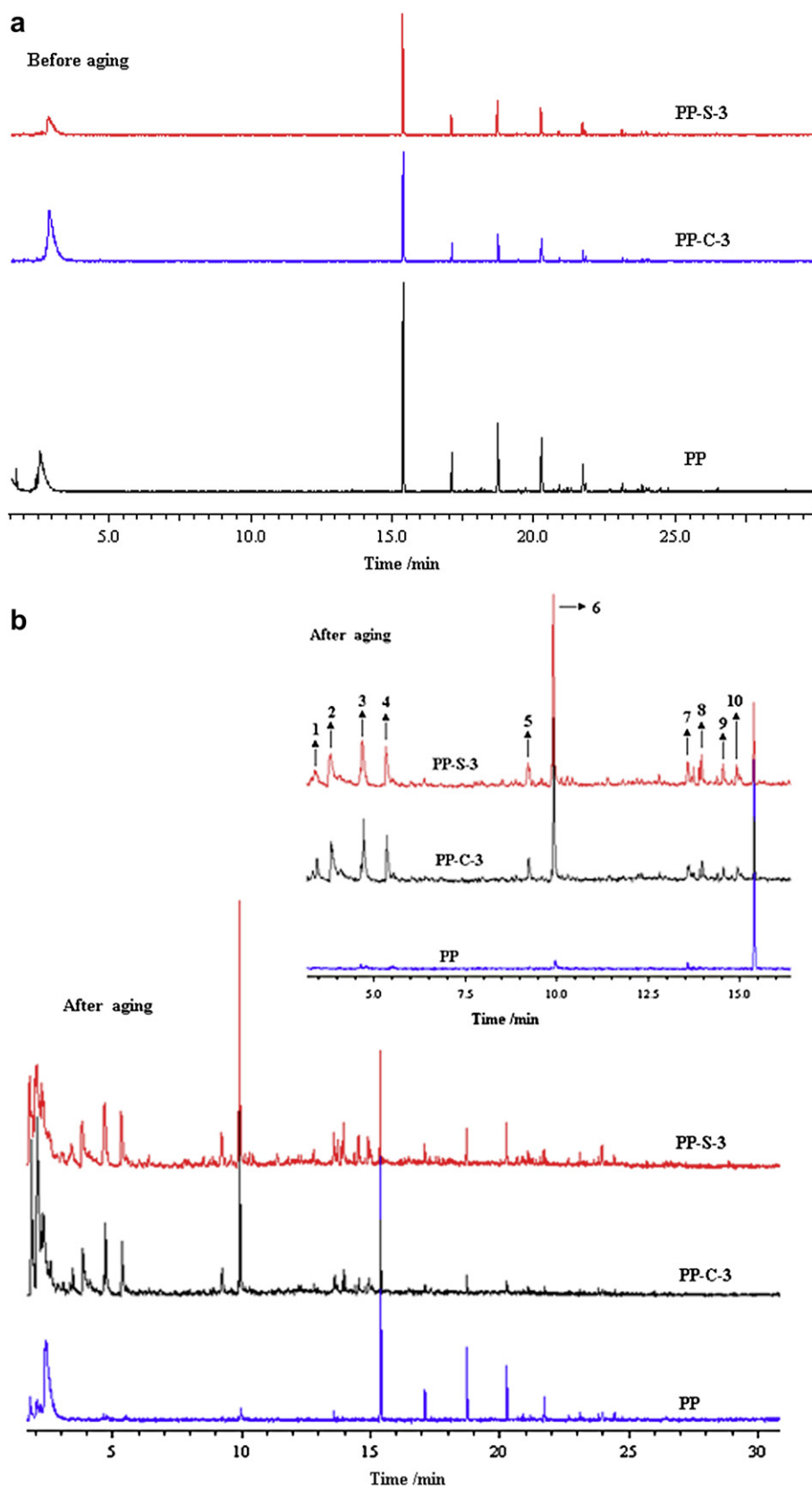


Fig. 4. PGC–MS pyrograms of PP and PP nanocomposites before and after exposure (the inlet shows the magnified range between 3 and 17 min).

40–60 days which might be due to the existence of minor antioxidant in the original samples.

The pyrolysis gas chromatography–mass spectroscopy (PGC–MS) analysis was carried out in order to investigate the volatile oxidation products after natural photo-oxidation (Fig. 4). Before natural aging, there were small molecules present in all samples, which were mainly attributed to alkanes with carbon number of 14–18 coming from the stearate added in the polymerization process. After exposure, there were many volatile oxygen-containing fragments and other small molecule fragments formed in PP nanocomposites. The structural information of these fragments are listed in Table 2. The main volatile oxidation products were ketones, esters and alcohols, and unsaturated double bonds, which is consistent with the results of FTIR. Large amount of output demonstrates the significant oxidation and chain scission of polypropylene. PP and PP nanocomposites having the same species of photo-oxidation products also suggested the same photo-oxidation mechanism although a quite low fragment amount appeared in PP.

PGC–MS results suggested the occurrence of chain scissions, which would certainly cause the reduction in molecular weight. The molecular weight and distribution changes before and after natural exposure are listed in Table 3. The value of weight-average molecular weight ( $M_w$ ), number-average molecular weight ( $M_n$ ) and polydispersity of PP and its nanocomposites all decreased greatly after exposure. For PP,  $M_n$  dropped to less than half of the original, and  $M_w$  decreased by about 1/3. The less reduction of  $M_w$  compared to  $M_n$  and broader distribution after exposure implies some crosslinkings took place as well as chain scissions. The crosslinked part increased the molecular weight and attributed more to  $M_w$ . With increased relative amounts of molecules at both higher and lower ends of the molecular weight range, the distribution was broadened. For PP-C-3 and PP-S-3, both the molecular weight and the distribution declined greatly. In PP-C-3,  $M_n$  decreased by 87% and  $M_w$  decreased by 92%. In PP-S-3,  $M_n$  decreased by 84% and  $M_w$  decreased by 92%. These results

Table 2  
Functional groups of characteristic peaks in Fig. 4

Peak number	Functional group
1, 8, 10	
2, 9	
3, 6	
4, 7	
5	

Table 3  
Molecular weight and polydispersity of PP and PP nanocomposites before and after natural photo-aging

Sample	PP-C-3		PP-S-3		PP	
	Before	After	Before	After	Before	After
$M_n$	52,000	7000	55,000	9000	63,000	30,000
$M_w$	309,000	24,000	300,000	24,000	351,000	229,000
Polydispersity	5.93	3.48	5.40	2.71	5.59	7.59

suggested the scissions of macromolecule chains and formation of smaller molecules. However, for PP nanocomposites, the chain scissions were predominant. Therefore, the polydispersities became narrower. The samples at the end of the tests were broken into pieces, and the basic mechanical properties were lost as well, due to such low molecular weight. The data in Table 3 also show that the blending procedure also causes some chain scissions of polypropylene, from about 350,000 in  $M_w$  of original PP to about 300,000 of PP nanocomposites.

Since nano fillers can serve as nucleation agents or impurities, they would certainly influence the crystallization of PP in nanocomposites. On the other hand, their effect on the oxidation and chain scission would also affect the chemi-crystallization during the photo-oxidation degradation. Therefore, the crystallinities of PP and its nanocomposites before and after exposure were determined by DSC (Table 4). Before the natural weathering, the addition of  $\text{CaCO}_3$  and  $\text{SiO}_2$  increases the crystallinity of PP a little. They serve as nucleation agents of PP. With higher filler content, the crystallinity is higher. After exposure, the crystallinities of all nanocomposites increased, trend as the same observed by Rabello and White [13,14]. This phenomenon is also due to the re-crystallization of small segments may generated by chain scission of tie molecules. However, the crystallinity of PP decreased a little after exposure although there were some chain scissions happened, which may also result in chemi-crystallization. Since crosslinking did not contribute to chemi-crystallization, the decreased crystallinity maybe mainly due to the surface erosion of some crystal phase by oxidation.

The results of FTIR, PGC–MS and HGPC showed that the pure PP and PP nanocomposites have the same natural photo-aging mechanism, and they are all caused by oxidation and chain scissions. However, what is the reason that the natural

Table 4  
Variation of the crystallinity of PP nanocomposites before and after exposure

Sample	Crystallinity (%)	
	Before aging	After aging
PP-C-1	36.3	38.4
PP-C-3	37.9	41.7
PP-C-5	39.9	41.0
PP-S-2	38.4	41.3
PP-S-3	38.9	43.6
PP	37.6	35.7

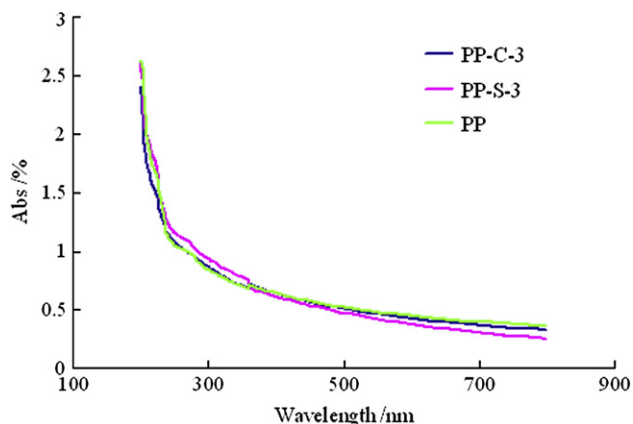


Fig. 5. The ultraviolet absorbance of PP and PP nanocomposites.

aging of PP nanocomposites was much faster than that of the pure PP? There may be several reasons for that:

- (1) Functional groups on the surface of nano particles catalyze the photo-oxidation reaction of PP. There are absorbed hydroxyl groups on the surface of the two nano fillers (more for nano-SiO<sub>2</sub>), which is active in photo-chemical reactions.
- (2) Poor adhesion of nano particles to PP matrix results in the agglomeration of nano particles in the matrix and interfacial failure under stress caused by the crystallization contraction. The effect of nano-SiO<sub>2</sub> is more significant because its compatibility to PP matrix is poorer, owing to a more hydrophilic surface with many hydroxyl groups on it.
- (3) Because the nano particle is proved to be a nucleation agent (see Table 4), it diminishes the spherulite size of PP. This would lead to more crystal interface. In addition to the amorphous region, the crystal surface is another favored photo-oxidation reaction site [15]. Furthermore, high interfacial tension at the interface may also induce the cracks.

Apart from the above reasons, the nano fillers may also help to absorb the sunlight, and serve as sensitizer of the photo-oxidation reaction of PP. The UV absorbances of PP and PP nanocomposites were determined (Fig. 5). It indicated that nano-CaCO<sub>3</sub> and nano-SiO<sub>2</sub> did not change the UV character

of PP obviously, and thus did not contribute to the higher oxidation degree of PP nanocomposites.

#### 4. Conclusions

The addition of nano-CaCO<sub>3</sub> and nano-SiO<sub>2</sub> into PP made the natural photo-oxidation much faster. The more the filler, the higher the oxidation rate. The photo-oxidation degradation of PP nanocomposites involved more oxidation and higher degree of chain scission compared to pure PP. However, the photo-degradation mechanism did not change significantly. The effects of nano-CaCO<sub>3</sub> and SiO<sub>2</sub> included several aspects: catalyzing to photo-oxidation reaction, nucleation effect, impurities, light sensitizers, etc. More detailed research on these factors should be carried out in the future.

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