

Preparation of Nanosilica-immobilized Antioxidant and the Antioxidation Effects in Polypropylene

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Abstract To improve the dispersion of silica in polypropylene (PP) matrix and to avoid physical loss of the antioxidants, nanosilica with dendric polyamidoamines on the surface (SG-PAMAM) was synthesized by using divergent method. Then nanosilica-immobilized antioxidant (SG-PAMAM-AO) was prepared by grafting 2,6-di-tert-butyl-4-aminophenol which was derived from 2,6-di-tert-butyl-4-phenol (AO). The SG-PAMAM-AO was added into PP by melt mixing to study the aging property. The oxidation induction time of PP/SG-PAMAM-AO and PP/AO compounds was measured. It was found that the antioxidant property of the SG-PAMAM-AO was superior to that of AO. According to the changes of carbonyl absorption before and after photo-thermal aging, the photo-thermal oxidative stability of PP/SG-PAMAM-AO was much higher than that of PP, PP/SG-PAMAM and PP/AO.

Keywords: Silica; Antioxidant; Polypropylene; Antioxidant behavior.

INTRODUCTION

Polypropylene (PP) is one of the most commonly used polymers due to the excellent mechanical properties and low cost. Compared to the pure PP, PP/silica composites have received much attention for their unique properties such as improved mechanical properties, increased transparency, enhanced gas barrier and reduced flammability^[1–6]. However, during the processing and application periods, PP and its composites suffer degradation caused by light, heat, oxygen and chemical agents. As a consequence, there appear deterioration of mechanical properties and reduced service life. Thus, many researches on degradation, including thermal oxidative degradation and photo oxidative degradation, have been carried out^[7–15].

The use of antioxidants in polymeric materials is an effective way for protection from thermal oxidative degradation. However, low molecular weight antioxidants are always subject to physical loss, such as volatilization, migration and water extraction. The physical loss of antioxidants leads to not only decreased performance of the polymeric materials but also pollution of the environment. To overcome these drawbacks, several methods have been developed. One method is increasing the molecular weight of antioxidants^[16, 17], which has been widely applied in industries. The second way is grafting reactive antioxidants onto the polymer backbone^[18–21]. The third approach is to attach antioxidants onto the nanoparticles^[22–24]. Nanosilica-immobilized antioxidant was proven to be effective in the stabilization of PP during the thermal aging^[23, 24].

Nanosilica is a promising inorganic filler for polymeric materials. It is covered with silanol groups, which make it acidic, moisture adsorbing and naturally hydrophilic^[25]. When it is added to polymers, it aggregates and makes the composite have decreased mechanical properties. To make full use of nanosilica as a reinforcing material, a wide variety of surface reactions to facilitate organic molecule attachment is carried out.

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In order to improve the dispersion of silica in PP matrix and to avoid physical loss of the antioxidants, a kind of new nanosilica with dendric polyamidoamines on the surface (SG-PAMAM) was synthesized through divergent method, and then used as solid support to immobilize reactive antioxidant onto the surface in this work. The nanosilica-immobilized antioxidant (SG-PAMAM-AO) was then incorporated into PP to evaluate the aging property. The short-term oxidation induction time of PP compounds was determined by DSC measurements. Accelerated photo-thermal aging experiments were carried out in an ultraviolet exposure instrument and the photo-thermal oxidative stability was evaluated by FTIR and TGA.

EXPERIMENTAL

Materials

Tetraethylorthosilicate (TEOS), ethylenediamine (EDA), methyl acrylate (MA), acetic acid, potassium persulfate, 2,6-di-tert-butyl-phenol (AO), and calcium chloride were all of analytical grade. γ -aminopropyl-trimethylsilane (APMS) was a commercial sample obtained from Wuhan University Silicone New Material Co., Ltd. The PP was supplied by Yanshan Petrochemical Co Ltd, Beijing, China. All other solvents and reagents were used as received.

Preparation of SG-PAMAM

Amino functional silica gel (SG-NH₂) was prepared according to the literature^[26]. 150 mL NaOH of 0.01 mol·L⁻¹, 3.8 mL APMS and 31.2 mL TEOS of 27.9% were added to a flask; the mixture was heated to 60 °C and then reacted for 24 h at nitrogen atmosphere. The solid product was filtered and then washed with methanol, then dried under vacuum at 60 °C over 24 h. The content of amino group of the silica was 1.458 mmol·g⁻¹ which was detected by elementary analysis.

A series of PAMAM dendrimers were synthesized by divergent method using the nanoscale SG-NH₂ as the core. The preparation of 0.5G SG-PAMAM was as follows: 10 g of SG-NH₂ and 22 mL of MA were added to a flask with 100 mL of methanol as solvent. The mixture was stirred at 50 °C for 24 h under a nitrogen atmosphere. The solid product was filtered, and washed using methanol, then dried under vacuum at 60 °C over 24 h.

The preparation of 1.0G SG-PAMAM was performed under a nitrogen atmosphere, a mixture of 8.0 g of 0.5G SG-PAMAM and 130 mL of EDA was stirred at 50 °C for 24 h in a flask with 100 mL of methanol as solvent. The product was filtered, and washed using methanol, then dried under vacuum at 60 °C over 24 h. Finally, 1.0G SG-PAMAM was obtained. By repeating the above steps, the higher generations of SG-PAMAM (1.5G and 2.0G) were synthesized. The generation of SG-PAMAM used in this study was 1.5G. The content of amino group of 1.0G SG-PAMAM was 1.614 mmol·g⁻¹ which was detected by titration with HCl aqueous solution.

Preparation of SG-PAMAM-OA

The Scheme for the synthesis of SG-PAMAM-AO is shown in Fig. 1. First, 2,6-di-tert-butyl-phenol was dissolved in petroleum ether at 30 °C, then the nitric acid of 30 wt% was dropped into the solution and reacted for 10 h at 30 °C. After cooling to room temperature, the crude product was washed by *n*-hexane for 3 times and rinsed with distilled water to neutral, dissolved in 0.5 mol/L sodium hydroxide, precipitated with concentrated hydrochloric acid, then vacuum filtered, washed and dried to give a pale yellow product of 2,6-di-tert-butyl-4-nitrophenol.

Subsequently, 2,6-di-tert-butyl-4-nitrophenol was dissolved in ethanol anhydrous under stirring. The calcium chloride of 8.5 wt% and zinc power was added into the solution when heated slightly, then the temperature of the mixture was raised to 80 °C and the reaction was kept at refluxing temperature for 8 h. After the reaction, the mixture was filtered while hot, and the filtrate was cooled in ice-water bath for 3 h, in which some red acicular crystals appeared gradually. It was then filtered, washed with distilled water, and dried in vacuum oven for 24 h at 40 °C to receive the 2,6-di-tert-butyl-4-aminophenol.

Accelerated Photo-thermal Aging Tests

The obtained PP films were placed in an aging test box and irradiated by a high pressure mercury lamp (250W) for photo-thermal aging. This device has been designed in order to accelerate the degradation of polymers in artificial conditions which are relevant to natural aging. The working temperature was regulated at $(40 \pm 5)^\circ\text{C}$ and the wavelength of radiation was about 300 nm. At appropriate time intervals, the samples were taken out and the changes due to photo-thermal oxidative degradation were monitored by FTIR (Perkin Elmer System 2000), and the aging behavior was evaluated by thermo gravimetric analysis (NETZSCH STA449C).

RESULTS AND DISCUSSION

Infrared Spectra

Figure 2 shows the FTIR spectrum of 2,6-di-tert-butyl-4-nitrophenol. The broad strong bands around 3546 cm^{-1} belongs to the stretching vibration of phenol hydroxyls and adsorbed water; the absorption at 3113 cm^{-1} is assigned to the C—H symmetric stretching of aromatic ring, and the bands around 2960 cm^{-1} and 2875 cm^{-1} are attributed to CH_3 asymmetric and symmetric stretches, respectively. The absorption around 1582 cm^{-1} is the characteristic of aromatic ring C=C, and the strong bands around 1510 cm^{-1} and $1335\text{--}1317\text{ cm}^{-1}$ are attributed to NO_2 asymmetric and symmetric stretches, respectively. The absorption at 1247 cm^{-1} is assigned to C—O stretches.

Figure 3 shows the FTIR spectrum of 2,6-di-tert-butyl-4-aminophenol. The band at 3640 cm^{-1} is assigned to the stretching vibration of phenol hydroxyls; the new absorption at 3326 cm^{-1} is assigned to the N—H stretching of aromatic amine, and the band around 2957 cm^{-1} is attributed to CH_3 asymmetric stretches. The absorption around 1609 cm^{-1} is the characteristic of aromatic ring C=C; the strong bands around 1393 cm^{-1} and 1362 cm^{-1} are attributed to tert-butyl bending, and the absorption at 1222 cm^{-1} is assigned to C—O stretches.

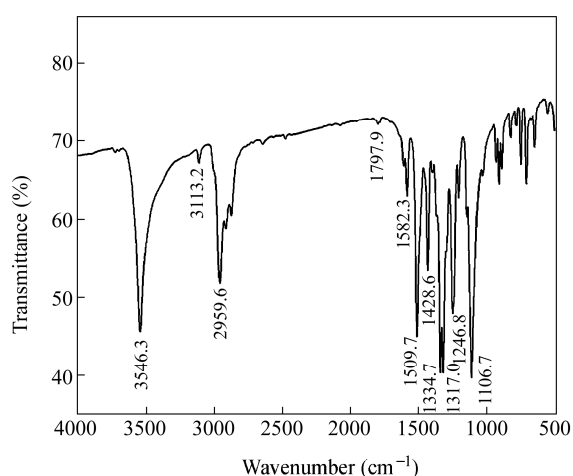


Fig. 2 FTIR spectrum of 2,6-di-tert-butyl-4-nitrophenol

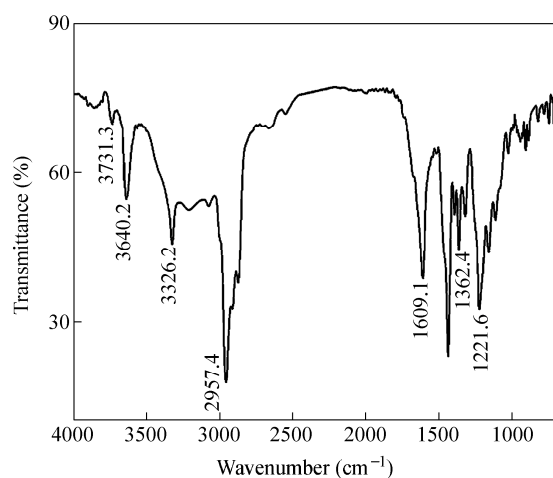


Fig. 3 FTIR spectrum of 2,6-di-tert-butyl-4-aminophenol

The FTIR spectra of SG-PAMAM and SG-PAMAM-AO are shown in Fig. 4. In SG-PAMAM, the broad bands around 3424 cm^{-1} are assigned to the N—H stretching vibration of amide, while the absorption around 1633 cm^{-1} is the characteristic of —C=O stretches of amide. In the ester-terminated SG-PAMAM, the absorption at 1745 cm^{-1} suggests the presence of ester bonds (—COOCH_3). The bands around 2936 cm^{-1} and 1460 cm^{-1} are the asymmetric stretching and bending of —CH_2 , respectively. The strong absorption at 1097 cm^{-1} is assigned to Si—O stretching vibration. Based on the above analysis, it is concluded that PAMAM was grafted successfully on the silica-gel surface.

In SG-PAMAM-AO, the absorption at 3618 cm^{-1} is attributed to the O—H stretching vibration of phenol hydroxyls. The broad bands around 3443 cm^{-1} and 1649 cm^{-1} are assigned to the amide groups. The absorption

around 1543 cm^{-1} is noticeable, which is the characteristic of the amide II. The strong absorption at 1074 cm^{-1} is assigned to Si—O stretching vibration. Another obvious characteristic on SG-PAMAM-AO is the enhanced amide stretch around 3443 cm^{-1} and the disappeared —NH_2 stretching of aromatic amine around 3326 cm^{-1} (in Fig. 3), which confirms chemical reaction between —NH_2 groups of the reactive antioxidant and ester groups on the SG-PAMAM surface. This result indicates that the hindered phenol antioxidant has been immobilized onto the SG-PAMAM nanosilica surface.

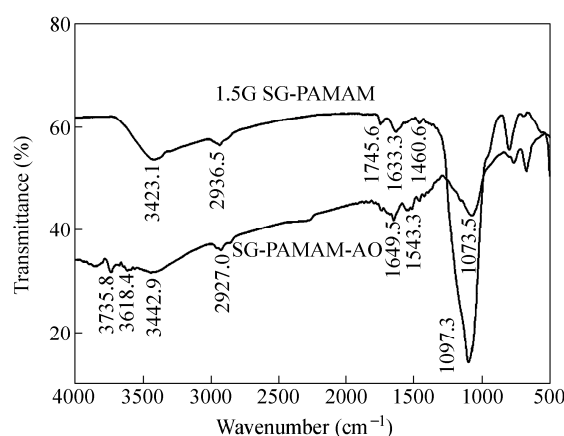


Fig. 4 FTIR spectra of 1.5G SG-PAMAM and SG-PAMAM-AO

Dispersion States of Nanosilica in PP Matrix

In general, there are large and non-uniformly dispersed silica particles with a particle size of 1–2 μm in PP/neat silica composite due to the aggregates and agglomerates of neat nanosilica. In contrast, AO-silica was homogeneously dispersed into the PP matrix on the nanometer scale^[24]. The morphology of SG-NH₂, SG-PAMAM and SG-PAMAM-AO is shown in Fig. 5. The original silica (SG-NH₂) and the modified silica (SG-PAMAM and SG-PAMAM-AO) had a particle size of 100–200 nm. The nanosilica particles presented irregular shape and agglomerated. Figure 6 shows the dispersion of SG-PAMAM and SG-PAMAM-AO in PP. It indicates that both the SG-PAMAM and SG-PAMAM-AO were uniformly dispersed in PP.

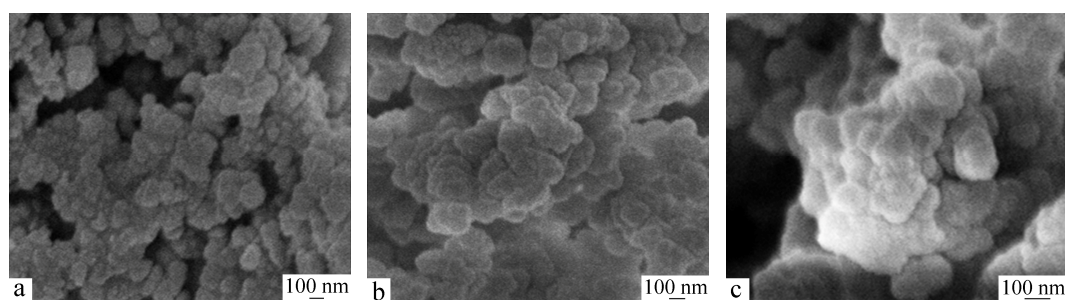


Fig. 5 SEM images of SG-NH₂ (a), SG-PAMAM (b) and SG-PAMAM-AO (c)

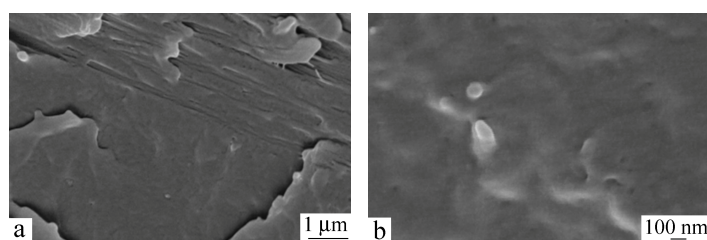


Fig. 6 SEM images of (a) PP/SG-PAMAM and (b) PP/SG-PAMAM-AO composites

OIT of PP Compounds

The OIT value determined by DSC was used to evaluate the thermal oxidative stability of polymeric materials. The more resistant the sample is to oxidative degradation, the longer the OIT value^[10]. Figure 7 shows the DSC curves of PP and PP compounds. The OIT values of PP, PP/SG-PAMAM, PP/SG-PAMAM-AO (1.0 g), PP/SG-PAMAM-AO (2.5 g) and PP/AO are 9.5, 8.3, 12.7, 11.5, 11.4 min, respectively. It shows that the SG-PAMAM had no contribution to the OIT value of polypropylene, but had weak affection on the thermal oxidative stability of PP due to the existence of polyamidoamines on the surface of nanosilica. The OIT values of PP/SG-PAMAM-AO are higher than those of pure PP, PP/SG-PAMAM and PP/AO compounds. This result indicates that the hindered phenol groups in SG-PAMAM-AO were obviously responsible for the exceptional antioxidant behavior^[24]. That means the SG-PAMAM-AO could provide good antioxidant property in PP compounds.

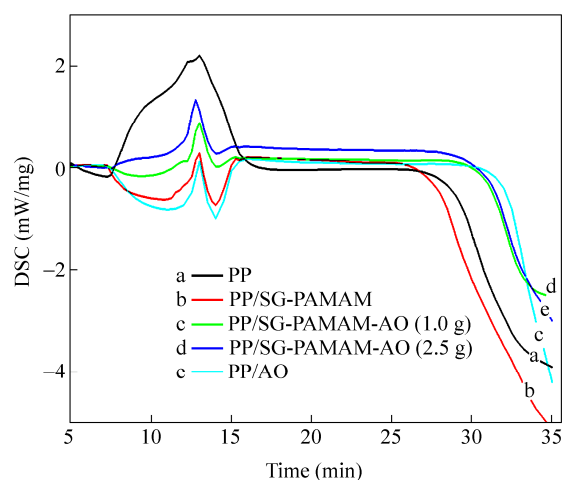


Fig. 7 OIT of PP and PP compounds (DSC measurement, 200 °C)

As a reference, the OIT value of PP/AO, containing an equivalent antioxidant in PP/SG-PAMAM-AO, is shorter than that of PP/SG-PAMAM-AO. One reason for the shorter OIT of PP/AO compound could be the volatilization of the antioxidant during the melt compounding because of its low molecular weight^[16, 22–24]. This result confirms that the antioxidant in SG-PAMAM-AO was non-volatile in polypropylene.

The OIT value of PP/SG-PAMAM-AO (2.5 g) was lower than that of PP/SG-PAMAM-AO (1.0 g) for the possible reason of the existence of PAMAM structure on the surface of SG-PAMAM. The content of PAMAM structure in PP/SG-PAMAM-AO (2.5 g) was more than that in PP/SG-PAMAM-AO (1.0 g). On the one hand, the PP/SG-PAMAM-AO (2.5 g) has the more AO structure content, which is benefit for the OIT values. On the other hand, the content of PAMAM structure is also increased, which may reduce the thermo stability of the composites.

Photo-thermal Oxidative Stability of Compounds

Infrared spectrometry is a powerful tool for studying the degradation of PP and several other polymeric materials in the solid states. The main thermal oxidative products of PP are the hydroperoxides and carbonyl species in the photo-thermal oxidation. The intensity of carbonyl and hydroxyl bands increases with increasing thermal aging time. Figure 8 gives the FTIR spectra of PP and its composites. As shown in Fig. 8(A), the intensity of carbonyl bands increased after 120 h photo-thermal oxidation, so the pure PP had obvious degradation. The PP/SG-PAMAM-AO did nearly not degrade during 120 h aging, but the PP/AO had certain degradation according to the intensity of hydroxyl bands in Fig. 8(B). It means that the SG-PAMAM-AO in PP compounds had good antioxidant efficiency. The difference of AO and SG-PAMAM-AO in antioxidant property is mainly due to physical loss. The low molecular antioxidant is easy to volatilize or migrate from the matrix to the surroundings.

Conversely, the antioxidant immobilized onto the silica surface was no longer migratory and volatile in the PP matrix^[24]. Thus the PP/SG-PAMAM-AO sample was more resistant to photo-thermal oxidation.

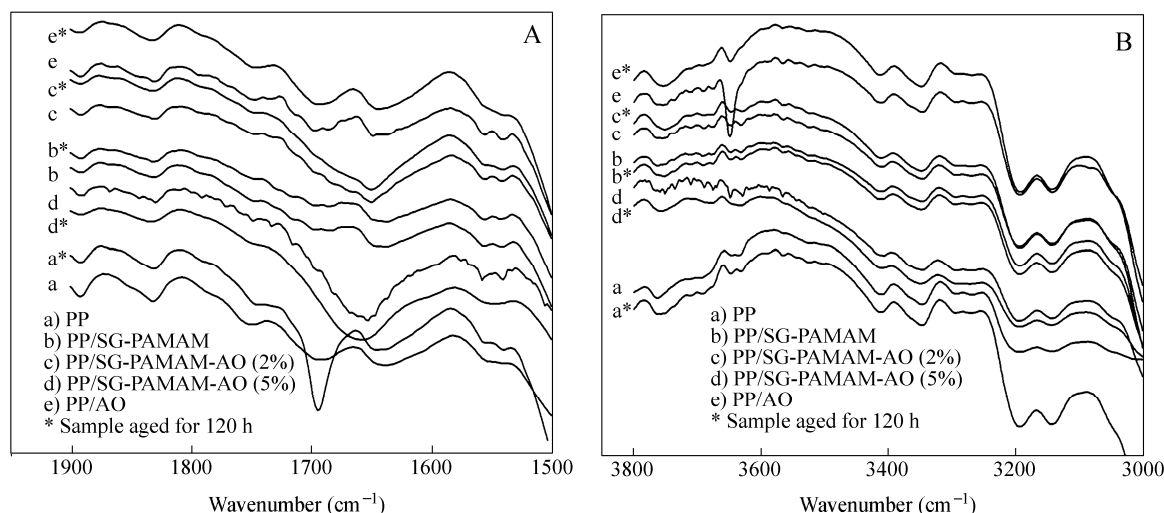


Fig. 8 FTIR spectra of PP and PP compounds (a) in the domain of 1900–1500 cm⁻¹ and (b) in the domain of 3800–3000 cm⁻¹

The results of TG analysis of PP and its compounds are given in Table 2. It can be seen that the pure PP had a low decomposition temperature (T_d). Obviously, the T_d of all the unaged samples are 20–30 K higher than that of their aged samples. The aging time (120 h) is not long, but it does have a relative obvious degradation. The T_d of PP compounds with additives are overall high than that of the pure PP, which indicates that the addition of the modified silica and antioxidant in PP may enhance the photo-thermal oxidative stability of the materials. In the case of PP/SG-PAMAM, the T_d was higher than the pure PP, which indicates that the presence of SG-PAMAM slightly inhibited the degradation of PP. It is probably due to the organic groups on the silica surface can interact with the hydroperoxides originating from the photo-thermal oxidative degradation of PP.

Table 2. TG analysis of the PP compounds

Sample	Content of additives (wt%)	T_d (°C)	
		Unaged	Aged (120 h)
PP	—	407.6	380.2
PP/SG-PAMAM	2.0	431.0	397.4
PP/SG-PAMAM-AO	2.0	430.7	411.4
PP/SG-PAMAM-AO	5.0	434.9	405.7
PP/AO	0.80	424.2	396.6

The T_d of PP/SG-PAMAM-AO (5%) was lower than that of PP/SG-PAMAM-AO (2%) for the possible reason of the more PAMAM structure in PP/SG-PAMAM-AO (5%) than in PP/SG-PAMAM-AO (2%). The more PAMAM structure means the more AO structure, but it would reduce the thermo stability of the composites, which is consistent with the results of the OIT values.

CONCLUSIONS

The nanosilica with dendritic polyamidoamines on the surface was synthesized by divergent method, then the nanosilica-immobilized antioxidant (SG-PAMAM-AO) was prepared by grafting 2,6-di-tert-butyl-4-phenol (AO). The SG-PAMAM-AO was homogeneously dispersed into the PP matrix by melt compounding. The OIT value of PP/SG-PAMAM-AO was higher than that of the PP/AO compound. FTIR and TG analysis confirmed that the SG-PAMAM-AO had much better antioxidant property in the PP composites compared to the low

molecular antioxidant during the photo-thermal aging. Therefore, this nanosilica-immobilized antioxidant is expected to be a new type of antioxidant with high performances such as non-volatile, non-migratory and non-lost during the aggressive service life.

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