

Preparation of nanosilica-immobilized antioxidant and the antioxidative behavior in low density polyethylene



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ABSTRACT

This article reports a study of the preparation of nanosilica-immobilized antioxidant (SiO₂-APTMS-AO) and the thermal oxidative stability of low density polyethylene (LDPE) nanocomposites containing SiO₂-APTMS-AO. SiO₂-APTMS-AO was prepared based on the fumed nanosilica which was firstly modified with an aminosilane coupling agent and then reacted with 3,5-Di-*tert*-butyl-4-hydroxybenzoic acyl chloride. Infrared spectroscopy, X-ray photoelectron spectroscopy and thermogravimetric analysis measurements confirmed that the antioxidant group was chemically immobilized onto nanosilica. LDPE/silica nanocomposites were prepared by melt mixing and then pressed into different films. The thermal oxidative stability of the nanocomposites was evaluated by thermogravimetric analysis in air atmosphere, oxidation induction time (OIT) and long-term accelerated thermal aging. The results showed that the SiO₂-APTMS-AO can significant improve the thermal oxidative stability of LDPE nanocomposite. Because SiO₂-APTMS-AO is based on inorganic nano-filler, in comparison to organic antioxidants, it might have advantages in thermal stability and migration stability during processing and application.

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1. Introduction

Low density polyethylene (LDPE) is mainly used in pipe industry, agricultural film, cable cover, commodity, packaging materials and other fields because of its advantage of easy manufacture, low thermal conductivity and good chemical resistance. Pure LDPE is regarded as a stable polymer and only slowly degradable in contrast to other polymers [1]. Because of the presence of impurities, hydroperoxides and carbonyl groups introduced during high-temperature manufacturing processing, LDPE becomes easy to be degraded under the influence of heat or UV-light [2,3]. Additives are usually added to prevent the degradation of LDPE, such as antioxidant, light stabilizers, antistatic agents et al. [4]. Hindered phenolic antioxidants are recognized as the most important long term heat stabilizer and widely used in LDPE. Because of the low molecular weight, low molecular weight antioxidants are easy to degrade or volatilize during polymer processing or likely to migration and extraction during their long-term usage [5–8]. In

recent years, Viebke, Gedde and coworkers have published a lot of research focused on this topic [9–13]. In order to overcome these drawbacks, several approaches that have been developed. One method is to increase the molecular weight of antioxidants. However, it was found that the high molecular weight of antioxidants, e.g. Irganox® 1010 or Irganox® 1076, also suffered from physical loss under aggressive service conditions [7,8,14]. Another approach is grafting the antioxidant groups onto the polymer backbone [15,16] or copolymerization of monomers with antioxidant-functionalized monomers [17]. Hindered phenol groups were utilized melt free-radical grafting to polyolefin. Recently, several new polymeric antioxidants were achieved by polymerization of monomer-bound via radical polymerization or via ring-opening metathesis polymerization (ROMP) [18–20].

In the recent years, modification of polymers by various nanoparticles have received considerable attention in both academia and industry due to their unique physical and/or chemical properties. In order to increase the thermal and thermo-oxidative stability, LDPE modified with various nanoparticles, e.g. layered double hydroxides [21–23], copper nanoparticles [24], silica [25,26], calcium carbonate [27], single wall or multiwall carbon nanotubes [22,28], layered silicates (clays) [29,30], POSS [31] etc. It

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was found that attach antioxidants onto the nanoparticles can dramatically improve the extraction resistance and achieve high stabilizing activity.

3,5-Di-*tert*-butyl-4-hydroxybenzoic acid is not a high efficiency antioxidant and often used as an intermediate to prepare other kinds of antioxidant and light stabilizer. In the present work, the immobilized antioxidant (SiO₂-APTMS-AO) was prepared by grafting 3,5-di-*tert*-butyl-4-hydroxybenzoic acid onto silica nanoparticle which acted as solid support. The chemical reaction and structure of SiO₂-APTMS-AO was investigated. The SiO₂-APTMS-AO was then incorporated into LDPE by melt processing. The antioxidative efficiency was evaluated by short-term oxidation induction time and long-term accelerated thermal aging. The experimental results have demonstrated that the SiO₂-APTMS-AO can effectively increase the thermal and thermo-oxidative stability of LDPE.

2. Experimental

2.1. Material

The low density polyethylene without stabilizer (LDPE 112A with a melt flow index of 2.0 g/10 min at 190 °C) was supplied by Yanshan Petrochemical Co LTD, Beijing, China. Aerosil-200 fumed nanosilica (SiO₂, surface area 200 ± 25 m²/g, primary particle size 12 nm, purity 98%) was obtained from Evonik Degussa, and dried in a vacuum oven overnight at 120 °C before use. Thionyl chloride, 3,5-di-*tert*-butyl-4-hydroxybenzoic acid and aminosilane coupling agent 3-aminopropyltrimethoxysilane (APTMS) were purchased from Alfa Aesar and used as-received. The toluene and pyridine were of analytical grade and used after distillation. All other solvents and reagents were used as-received.

2.2. Preparation of functionalized nanosilica

The aminosilane coupling agents modified nanosilica, SiO₂-APTMS, was synthesized as illustrated in Scheme 1. The experimental details have been described in our previous work. The SiO₂-APTMS was dried in a vacuum oven overnight at 120 °C.

3,5-Di-*tert*-butyl-4-hydroxybenzoic acid (AO, 5.0 g) was dissolved in thionyl chloride (20 mL) and the reaction mixture was allowed to reflux until no hydrochloric acid was generated. Then removed the unreacted thionyl chloride by evaporated under reduced pressure. The obtained product was added to the suspension of SiO₂-APTMS (5.0 g) in anhydrous toluene (200 mL) under stirring. Anhydrous pyridine (1.0 mL) was next added drop wise and the mixture was stirred for 24 h at room temperature under nitrogen atmosphere. The obtained product was filtered and washed with anhydrous toluene (200 mL, 3 times) and absolute ethanol (200 mL, 3 times). The nanosilica-immobilized antioxidant

(SiO₂-APTMS-AO) was dried in a vacuum oven overnight at 120 °C.

2.3. Preparation of LDPE/silica nanocomposites

The LDPE/silica nanocomposites were prepared by melt blending using an HAAKE PolyLab OS RheoDrive 7 (Thermo Fisher Scientific, Germany) at 180 °C with a low rotor speed of 20 rpm for the first 2 min for preheating then with a high rotor speed of 50 rpm for another 5 min for complete mixing. Prior to the melt blending, the fumed nanosilica and functionalized nanosilica were dried in a vacuum oven overnight at 120 °C. Several LDPE compounds were prepared and their compositions are listed in Table 1. In LDPE/AO composite, the AO content is 0.31 wt%, equivalent to the molar fraction of the antioxidant in LDPE/SiO₂-APTMS-AO nanocomposite. The prepared materials were pressed into films at 180 °C with an average thickness of 260 μm for TGA and DSC measurements and 40 μm for accelerated aging test.

2.4. Accelerated aging test

The obtained LDPE films (40 μm) were placed in an air oven at 90 °C for thermal aging. At appropriate time intervals, the samples were taken out from the oven and the changes due to thermal oxidative degradation were monitored by Infrared spectroscopy (IR) tests. A Perkin–Elmer System 2000 infrared spectrometer was used to measure the structural changes of LDPE films. Carbonyl index (CI), as determined from IR spectra was used to characterize the extent of degradation of LDPE molecular. It was calculated by Eq. (1)

$$\text{Carbonyl index} = A_C/A_R \quad (1)$$

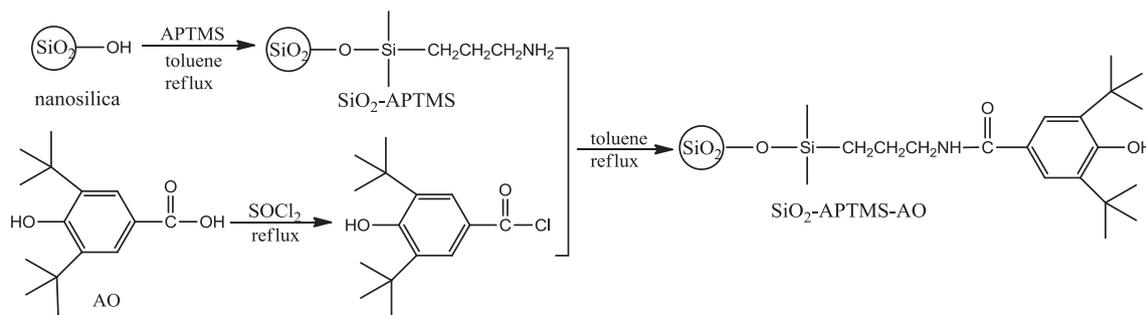
where A_C is the area of the carbonyl absorption band around 1723 cm⁻¹ and A_R is the area of the reference band around 1463 cm⁻¹ [32].

2.5. Characterizations

IR analysis was carried out using a Perkin–Elmer System 2000 infrared spectrum analyzer in the wave number range of

Table 1
LDPE and LDPE/silica nanocomposites and their compositions.

Sample	Type of additives	Content of additives (wt%)
LDPE	–	–
LDPE/SiO ₂	SiO ₂	3.0
LDPE/SiO ₂ -APTMS	SiO ₂ -APTMS	3.0
LDPE/AO	AO	0.31
LDPE/SiO ₂ -APTMS-AO	SiO ₂ -APTMS-AO	3.0



Scheme 1. Synthesis of functionalized nanosilica (SiO₂-APTMS-AO).

4000–650 cm^{-1} with KBr pellets.

X-ray photoelectron spectroscopy (XPS) data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Al $K\alpha$ radiation. The base pressure is about 3×10^{-9} mbar. The binding energies are referenced to the C1s line at 284.6 eV from adventitious carbon.

Thermogravimetric analysis (TGA) was carried out using a Perkin-Emler Pyris 1 thermogravimetric analyzer in nitrogen atmosphere and a Perkin-Emler TGA-7 thermogravimetric analyzer in air atmosphere. The thermal behavior of the functionalized silica in nitrogen atmosphere from 50 °C to 750 °C at a heating rate of 20 °C/min. The thermal behavior of LDPE samples was performed under air atmosphere from 50 °C to 650 °C at a heating rate of 20 °C/min.

Scanning electron microscope (SEM) images were taken on a JEOL S4300F field emission scanning electron microscope at 5 kV. The fracture surfaces of the sample were generated by a strong force in liquid nitrogen. The fracture surfaces of the broken pieces were coated with Pt to enhance the conductivity before the SEM observation.

A Perkin-Emler DSC 7 according to the standard method (ISO 11357-6, 2002) to evaluate the oxidation induction time (OIT) of LDPE/silica nanocomposites. The method used for the OIT test has been described in our previous paper. At first, the sample was held at 60 °C for 5 min with a nitrogen flow of 50 mL/min. Then, the sample was heated to 210 °C at a rate of 20 °C/min. After reaching 210 °C, the sample was held for another 5 min for equilibration, at which point the gas was switched to oxygen at a flow rate of 50 mL/min. The oxidation of the sample was observed as a sharp increase in heat flow due to the exothermic nature of the oxidation reaction. The OIT was obtained by the software of Perkin-Emler DSC 7.

3. Results and discussion

3.1. Immobilization of the antioxidant group onto nanosilica

Like immobilization of the UV absorber group onto the surface of nanosilica particles, three steps reaction were taken to create chemical bonding between the antioxidant group and the nanosilica particle [33]. The surface of nanosilica first modified with APTMS to obtain SiO_2 -APTMS. Then, by the reaction of acylation, chloro-acetylated antioxidant was made. Finally, SiO_2 -APTMS-AO can be synthesized by amino groups on the surface of nanosilica reacted with acyl chloride groups of chloro-acetylated antioxidant. The route of direct reaction between nanosilica and chloro-acetylated antioxidant are not effective and was not used.

Fig. 1 shows the IR spectra of fumed nanosilica, SiO_2 -APTMS and SiO_2 -APTMS-AO. In the fumed nanosilica, we can observe the asymmetrical stretching vibration peaks of Si–O–Si reaches near 1100 cm^{-1} , the bending vibration near 810 cm^{-1} of Si–OH (silanol). In SiO_2 -APTMS, the bands around 2931 cm^{-1} and 2878 cm^{-1} are attributed to CH_2 asymmetric and symmetric stretches, respectively, and absorption at 1480 cm^{-1} is the characteristic of CH_2 bending. The absorption at 1560 cm^{-1} is assigned to N–H bending. In SiO_2 -APTMS-AO, the absorption of amide II at 1545 cm^{-1} can be observed, which confirms chemical reaction between the acyl chloride groups of chloro-acetylated antioxidant and the $-\text{NH}_2$ groups on the SiO_2 -APTMS surface. The absorption at 2965 cm^{-1} corresponds to the enhanced CH_3 asymmetric stretch, which can be assigned to the *tert*-butyl groups of the hindered phenol antioxidant.

X-ray photoelectron spectroscopy (XPS) technique is a very useful tool for chemical surface analysis. Fig. 2a–b depicts the N 1s binding energy in SiO_2 -APTMS and SiO_2 -APTMS-AO were performed by XPS measurement. From Fig. 2a, N spectrum can be

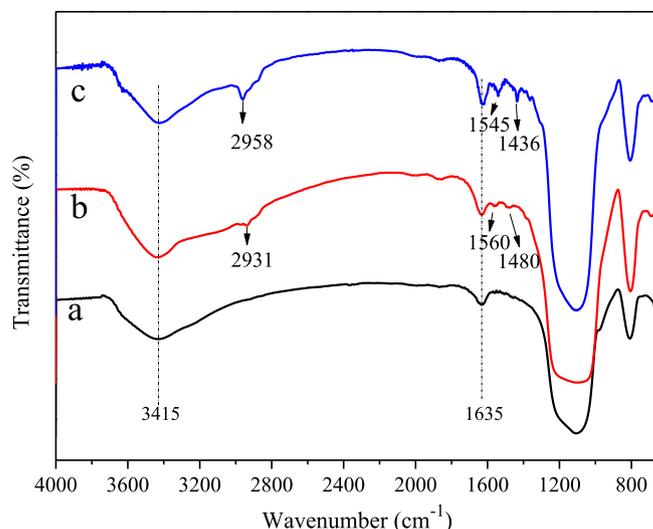


Fig. 1. IR spectra of (a) fumed nanosilica, (b) SiO_2 -APTMS and (c) SiO_2 -APTMS-AO.

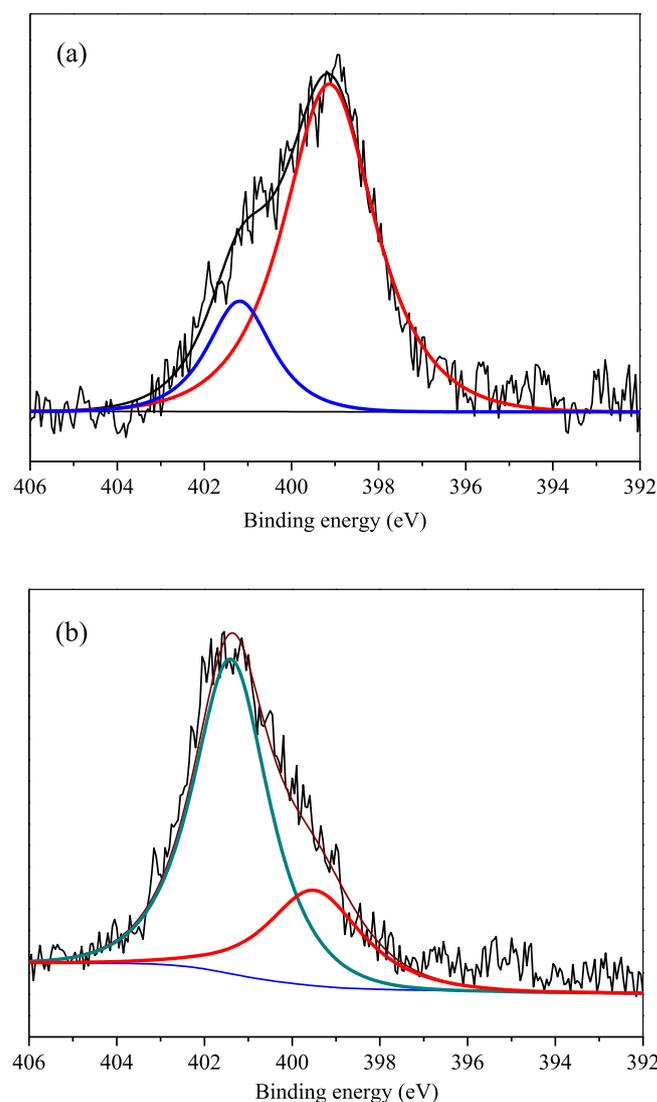


Fig. 2. XPS spectra of (a) SiO_2 -APTMS and (b) SiO_2 -APTMS-AO in the N1s region.

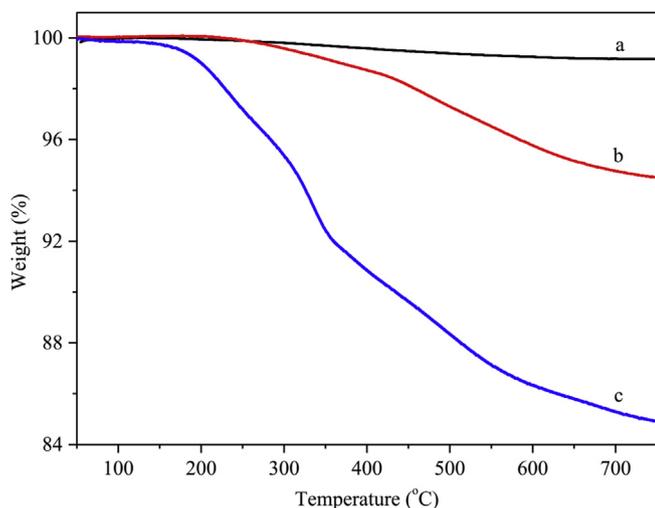


Fig. 3. TG curves of (a) fumed nanosilica, (b) SiO₂-APTMS and (c) SiO₂-APTMS-AO in nitrogen atmosphere.

divided into two peaks, an intense peak at 399.0 eV and a weak shoulder peak at 410.0 eV. The low binding energy corresponds to the free amine group ($-\text{NH}_2$) from APTMS and the high binding energy originates from the protonated amines ($-\text{NH}_3^+$) [26]. As shown in Fig. 2b, two signals could be resolved at binding energy of 399.5 eV and 401.4 eV. The low binding energy 399.5 eV was attributed to the characteristic of residual $-\text{NH}_2$ group. The high binding energy was assigned to amide ($-\text{NH}-(\text{C}=\text{O})-$) characteristic in SiO₂-APTMS-AO. Therefore, the XPS results further confirmed that the reactive antioxidant group was chemically immobilized onto the surface of nanosilica.

The results of the thermogravimetric analysis (TGA) of fumed nanosilica, SiO₂-APTMS and SiO₂-APTMS-AO are presented in Fig. 3. Based on the weight losses of SiO₂-APTMS and SiO₂-APTMS-AO from 150 °C to 750 °C, the loading of functionalized groups is 10.2 wt% on SiO₂-APTMS-AO.

3.2. Dispersion states of nanosilica in LDPE matrix

The dispersion states of fumed nanosilica and functionalized nanosilica in LDPE were observed by SEM, as shown in Fig. 4. It is easily observed large and non-uniformly dispersed nanosilica particles in LDPE/SiO₂ composite (Fig. 4a), with a size of 1–2 μm. It indicated that the aggregates and agglomerates of fumed nanosilica were not separated by melt blending. The morphology of LDPE/SiO₂-APTMS is shown in Fig. 4b. The aminosilane coupling agents modified nanosilica, SiO₂-APTMS in LDPE matrix is basically homogenous but there still are some aggregates with a size of 0.5 μm. On the contrary, the SiO₂-APTMS-AO was characterized by a much smaller size (about 100–200 nm) and uniform distributed in LDPE matrix on the nanoscale (Fig. 4c).

3.3. Thermal properties of LDPE/silica nanocomposites

The thermal properties for both LDPE/silica nanocomposites and pure LDPE was investigated by TGA in air atmosphere. The TGA and DTG curves are shown in Fig. 5a and b, and the selected data are listed in Table 2. As shown in Fig. 5 and Table 2, the thermal decomposition for LDPE/AO composite occurs at a higher temperature, but at a faster rate than pure LDPE and the other systems. This could be because AO can prevent the degradation of LDPE composites in the initial duration, however, as the temperature rises, the degradation of LDPE composites can be accelerated by AO as a kind of acid. It can be seen that nanosilica filled composites

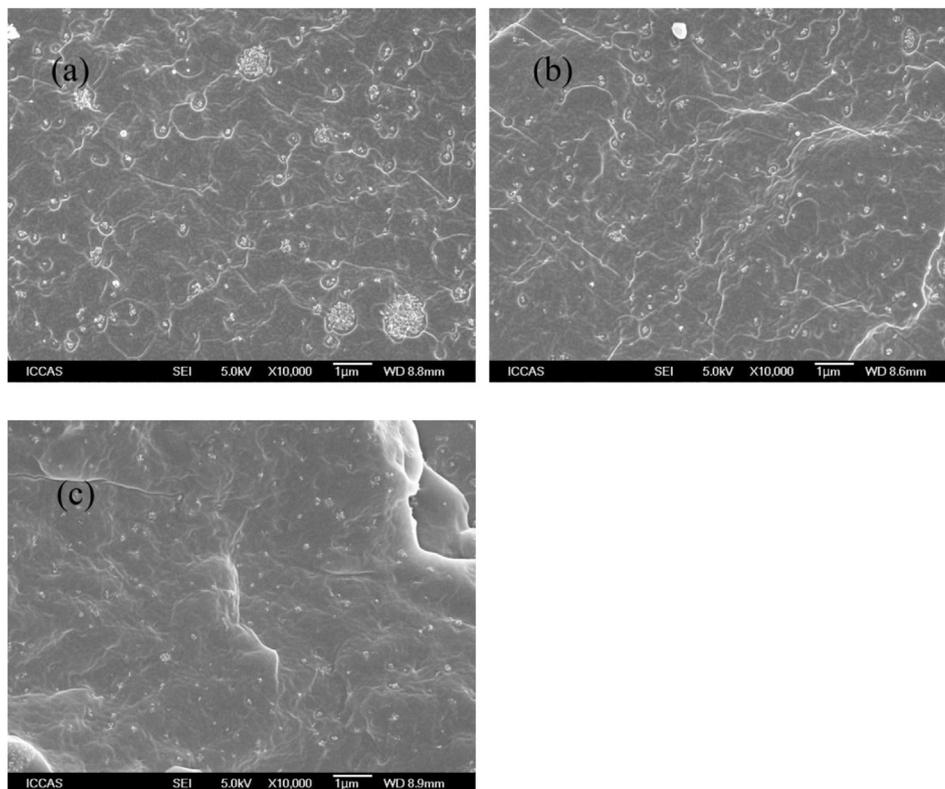


Fig. 4. SEM images of (a) LDPE/nanosilica, (b) LDPE/SiO₂-APTMS and (c) LDPE/SiO₂-APTMS-AO.

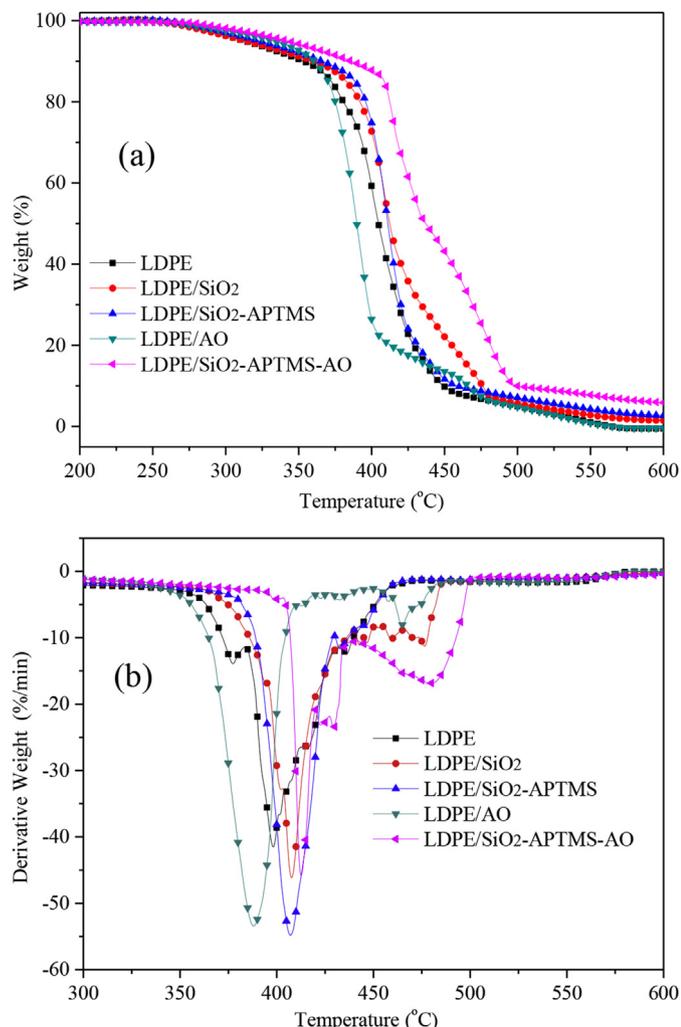


Fig. 5. TG (a) and DTG (b) curves of LDPE and LDPE/silica nanocomposites in air atmosphere.

Table 2
The select data of LDPE and LDPE/silica nanocomposites in air atmosphere.

Sample	T _{1%} (°C)	T _{5%} (°C)	T _{50%} (°C)	T _{max} (°C)
LDPE	271	313	405	398
LDPE/SiO ₂	267	314	412	408
LDPE/SiO ₂ -APTMS	276	323	411	407
LDPE/AO	273	335	390	388
LDPE/SiO ₂ -APTMS-AO	285	343	437	412

show enhanced thermal stability than pure LDPE. Both SiO₂ and SiO₂-APTMS can improved the decomposition temperature (temperature at 5% weight loss) of LDPE composites. SiO₂-APTMS-AO can significantly improve the thermal stability of LDPE composites. That is to say, SiO₂-APTMS-AO was much more efficient that SiO₂ or SiO₂-APTMS in preventing thermo-oxidative degradation of LDPE composites. It was obvious that the hindered phenol groups of the SiO₂-APTMS-AO was most responsible for the exceptional thermo-oxidative stability behavior.

3.4. Oxidation induction time of LDPE/silica nanocomposites

The oxidation induction time (OIT) determined by DSC has been considered as a measurement of check the efficiency of the

stabilizers or stabilizing systems in the melt states. Especially for polyolefin, OIT measurements are well established as a quick screening method to check the activity of the stabilization system used. The higher the thermo-oxidative stability of sample is, the longer of OIT value is. Fig. 6 shows the DSC curves of LDPE/silica nanocomposites. According to the DSC curves, it can be seen that LDPE and LDPE/SiO₂ composites were immediately detected the oxidative degradation as the atmosphere was changed from nitrogen to oxygen. It indicated that fumed nanosilica had no contribution to the OIT values of LDPE composites. The OIT value of LDPE/SiO₂-APTMS composite is less than 1 min, a little higher than LDPE, which revealed APTMS had little effect on thermo-oxidative degradation of LDPE. For LDPE/AO composites, the OIT values are about 4 min. The value is very low, that showed the AO, 3,5-Di-*tert*-butyl-4-hydroxybenzoic acid used in LDPE/AO composite is inefficiency. The reason could be 3,5-Di-*tert*-butyl-4-hydroxybenzoic acid is a kind of acid, which affects its efficiency. Another reason could be the volatilization of antioxidant during the melt blending because of its low molecular weight. The OIT value of LDPE/SiO₂-APTMS-AO composite is 29 min, much higher than those of LDPE, LDPE/SiO₂, LDPE/SiO₂-APTMS and LDPE/AO compounds. This result revealed that the SiO₂-APTMS-AO was much higher efficient than neat nanosilica and SiO₂-APTMS in preventing thermo-oxidative degradation. It is evident that the hindered phenol group of SiO₂-APTMS-AO was most responsible for the antioxidative behavior. In our previous work, the OIT value of LDPE/AO-AEAPS-silica is 45 min by DSC measurement in 200 °C [26]. In contrast, the OIT value of LDPE/SiO₂-APTMS-AO is 29 min in 210 °C and too long (more than 60 min, out of the limit of the test standard) in 200 °C. This may be because the C=C bond in the structure of AO-AEAPS-silica affects the thermal stability of LDPE/AO-AEAPS-silica composite.

3.5. Thermal oxidative stability of LDPE/nanosilica composites during long-term accelerated aging

Infrared spectrometry is one of the most common methods to study the molecular structure and functional group, so it is a powerful tool for studying the degradation of low density polyethylene and several other polymeric materials in the solid states. Fig. 7 shows the IR spectra of the films of LDPE after thermal aging for different times. The significant changes of spectra occurred in carbonyl (1680–1780 cm⁻¹), amorphous (1300 cm⁻¹) and hydroxyl regions (3400 cm⁻¹). Evidence of acid (1713 cm⁻¹), ester (1735,

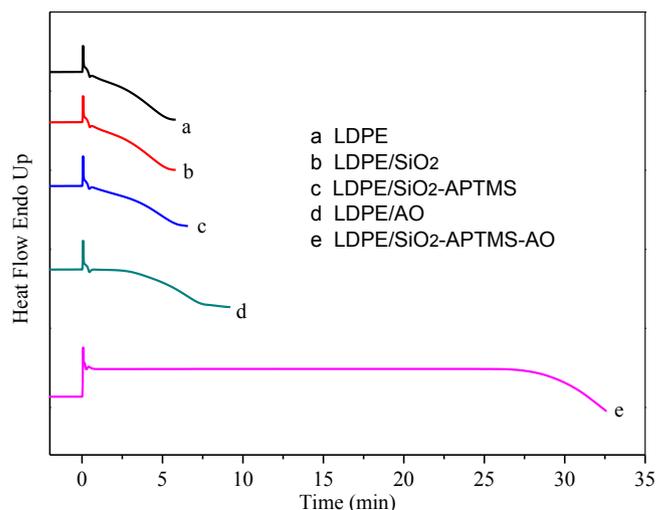


Fig. 6. Determination of OIT (DSC measurement, 210 °C).

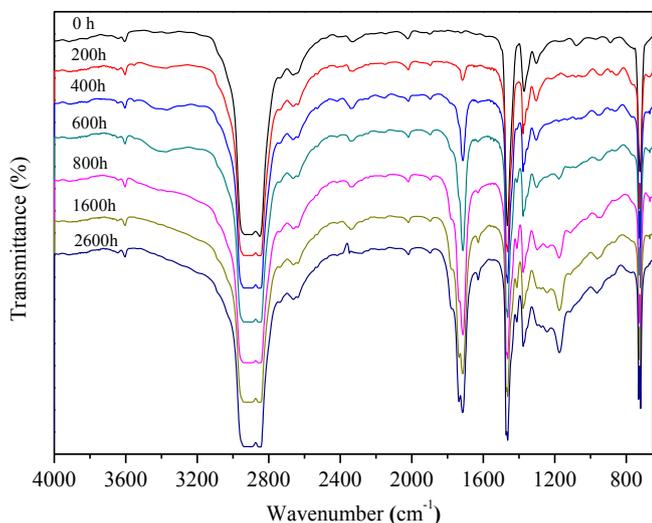


Fig. 7. IR spectra of the films of LDPE after thermal ageing (90 °C) for different times.

1242 and 1175 cm^{-1}), lactone (1783 cm^{-1}), ketone (1715 and 1412 cm^{-1}), hydrogen bonded OH (3300–3500 cm^{-1}) and vinyl groups (1628 cm^{-1}) are formed during the thermal oxidation processes [34–36]. Fig. 8 shows the IR spectra of the films of LDPE/silica nanocomposites in carbonyl and amorphous regions after thermal ageing for 2600 h. As shown in Fig. 8, the IR spectra of LDPE/SiO₂-APTMS-AO only have a slight absorption in the region of 1680–1760 cm^{-1} and little absorption in 1628 cm^{-1} , 1412 cm^{-1} and 1175 cm^{-1} . The results indicating that the degrees of degradation of the LDPE/SiO₂-APTMS-AO nanocomposite is much less than other LDPE composites.

In order to obtain a more quantitative expression for the extent of the thermal degradation, the carbonyl index (CI) for LDPE/silica nanocomposites after different thermal aging time is shown in Fig. 9. As shown in Fig. 9, the LDPE started to degradation not more than 300 h thermal oven aging. The LDPE/AO composite started to degradation at about 400 h, which indicated the presence of the low molecular AO slightly inhibited the degradation of LDPE. The LDPE/SiO₂ and LDPE/SiO₂-APTMS did not degrade until after 500 h and 600 h, respectively. This result may be because that there exists an

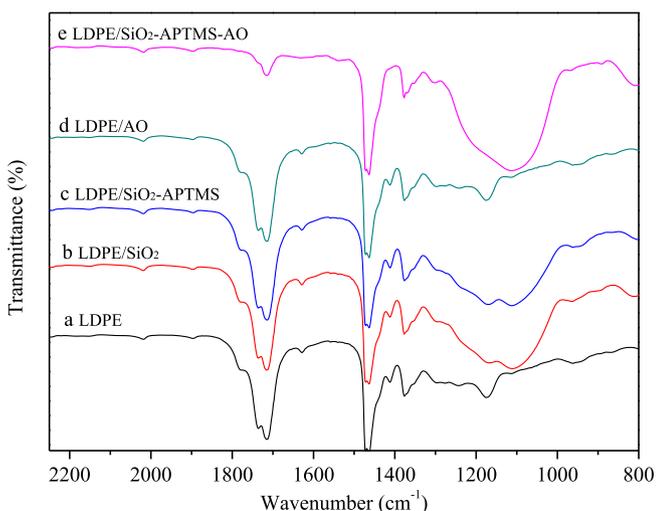


Fig. 8. IR spectra of the films of LDPE/silica nanocomposites after thermal ageing (90 °C) for 2600 h in the domain 2200–800 cm^{-1} .

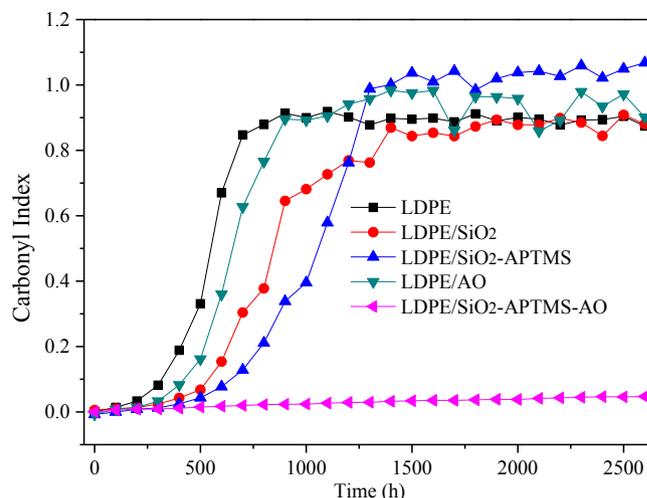


Fig. 9. Carbonyl index versus thermal aging (90 °C) of LDPE/nanosilica composites thin films.

energy barrier during the long-term accelerated aging of nanosilica. In addition, the amino groups in the SiO₂-APTMS can interact with the hydroperoxides originating from LDPE degradation. The CI values of LDPE/SiO₂-APTMS-AO nanocomposite increased slowly and still very small after 2600 h thermal aging. It means that the antioxidant efficiency of SiO₂-APTMS-AO is very high in long-term accelerated aging. The huge difference of thermal stability of LDPE/AO and LDPE/SiO₂-APTMS-AO composite might be because the carboxyl group in 3,5-di-*tert*-butyl-4-hydroxybenzoic acid was eliminated in SiO₂-APTMS-AO. As shown in TGA measurement, 3,5-di-*tert*-butyl-4-hydroxy-benzoic acid can prevent the degradation of LDPE composites in the initial duration, however, as the temperature rises, the degradation of LDPE composites can be accelerated by AO as a kind of acid. These results are in good accordance with the previous results obtained by TGA and DSC measurements.

4. Conclusion

In this paper, the reactive antioxidant (3,5-di-*tert*-butyl-4-hydroxybenzoic acid) was successfully immobilized onto the surface of nanosilica particles via the aminosilane coupling agent, which have been confirmed by IR, XPS and TGA. A melt processing method has been used to prepare LDPE/silica nanocomposites. The SiO₂-APTMS-AO was homogeneously dispersed in the matrix of LDPE. The thermal properties of LDPE/silica nanocomposites were investigated by TGA in air atmosphere. SiO₂-APTMS-AO can significantly improve the thermal stability of LDPE composites. The oxidation induction time of LDPE/silica nanocomposites was determined by DSC measurement. The OIT value of LDPE/SiO₂-APTMS-AO nanocomposite was much higher than LDPE/AO composite. The long-term thermal aging test of LDPE/silica nanocomposites was carried out in the air oven at 90 °C and the aging behavior was evaluated by IR test. The IR results confirmed that SiO₂-APTMS-AO showed much better antioxidant efficiency in the LDPE/silica nanocomposites compared to the corresponding low molecular counterpart.

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