



Anti-aging behavior of amino-containing co-condensed nanosilica in polyethylene



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ABSTRACT

Physical loss of stabilizers by migration and extraction accelerates the degradation of polymer materials. In this work, amino-containing nanosilica with anti-aging properties was prepared simply by the co-condensation of tetraethoxysilane and *N*-(2-aminoethyl)-3-aminopropyl-trimethoxysilane (AEAPS). AEAPS was used to introduce amino groups into silica nanoparticles and to act as a catalyst in this process. The co-condensed nanosilica (CCS) showed agglomerate structure similar to the typical fumed nanosilica (FS). The amino groups were distributed both on the surface and inside the nanoparticles. HDPE/CCS and HDPE/FS composites were prepared by melt blending. Thermogravimetric analysis and oxidative induction time showed that CCS has effectively improved the thermo-oxidative stability of HDPE. In the long-term accelerated thermo-oxidative aging and UV aging tests, HDPE/CCS composite showed superior stability to neat HDPE and HDPE/FS composite. The results of infrared spectroscopy and electron paramagnetic resonance suggested that the HDPE/CCS composite manifested a special degradation mechanism involving the nucleophilic addition of amino groups to carbonyl species as well as the oxidation of amino groups on CCS by peroxides. The amino groups on CCS consumed carbonyl species and peroxides, and generated hydroxylamines and nitroxide radicals which were able to eliminate free radicals, thus restrained the degradation of HDPE.

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1. Introduction

Polymer materials are vulnerable to heat, light and oxygen, which cause inevitable degradation during their processing, usage and storage and lead to the deterioration of their performances. Additives such as antioxidants and light stabilizers are often added to prolong their service life.

Hindered amines like 2,2,6,6-tetramethylpiperidine are high efficiency light stabilizers. It was found that the amino groups in piperidine rings could be easily transferred to stable nitroxide radicals which were excellent alkyl radical scavengers. The

nitroxide radicals were able to regenerate in a cyclic reaction which involves the formation of alkoxyamines [1,2]. Though the regeneration mechanism is still no consensus, it is generally accepted that the regeneration cyclic are responsible for the scavenging of alkyl and peroxy radicals [1–6]. Aromatic amines are effective electron-donor chain breaking antioxidants. Different from hindered phenol antioxidants, aromatic amines are able to generate nitroxide radicals to scavenge alkyl radicals as an electron-accept chain breaking antioxidants [7–9].

Aliphatic amines also showed antioxidant effect. It was found that thermo-oxidative stability of amine-grafted polypropylene copolymers was better than that of corresponding non-grafted copolymers [10]. Lignin amine modified polyurethane showed improved anti-aging performance and mechanical properties than unmodified polyurethane [11]. Amino-modified nanosilica could effectively retard the thermal oxidation and UV oxidation of polypropylene [12]. Amino-modified buckminsterfullerene even presented comparable antioxidant efficiency with commercialized

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aromatic amine antioxidant [13]. In spite of the relatively poor intrinsic anti-oxidative efficiency, aliphatic amines exhibited great synergistic effect with phenol and hindered amine stabilizers [14,15]. It was suggested that aliphatic amines could react with aldehydes to form imines or enamines, thus prevent the formation of peracids and restrain the acceleration of polypropylene oxidation [15].

Low molecular weight stabilizers suffered from physical loss by migration and extraction, which constituted a major concern in the environmental issues and safety regulation [16–21] as well as in the long-term use of polymers [22–34]. Researches were conducted to graft hindered phenols [35–41], hindered amines [13,42], aromatic amines [43–46], mercaptobenzimidazole [47,48] or some natural antioxidants [49,50] onto nanoparticles such as silica [35–38,43–50], titanium dioxide [42], carbon nanotubes [39–41], fullerene [13] and graphene oxide [51,52] to improve the resistance of the antioxidants to migration and extraction. However, sometimes the grafting weakens the stabilization efficiency due to the reduced mobility and the deactivating effect of nanoparticles [38,53]. The application of the antioxidant-grafted nanoparticles is still under developing refers to the multiple reactions, time and energy consuming and the usage of toxic solvents.

In the perspective of fillers, many unmodified fillers like silicate minerals [54] and silica [53,55] are necessary in improving mechanical properties. But they have none effect or even harmful on the UV stability of polymeric materials. Endowing fillers with anti-aging properties is helpful to design polymer materials with perfect mechanical properties as well as good weathering resistance.

As an alternative approach, amino-containing nanosilica was prepared simply by the co-hydrolysis and co-condensation of tetraethoxysilane and *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane in this work. The anti-oxidative efficiency of the co-condensed nanosilica (CCS) in high density polyethylene (HDPE) during short-term oxidation was evaluated by thermal gravimetric analysis and oxidative induction time. The long-term thermo-oxidative aging and UV aging of HDPE/CCS composites was assessed by the change of carbonyl band monitored with IR. The anti-aging mechanisms of CCS as well as the interaction between amino group and polyethylene during aging process were discussed.

2. Experimental

2.1. Materials

Aerosil®-200 fumed nanosilica (FS, primary particle size 12 nm, purity 99.8%) was purchased from Evonik Degussa, and dried in vacuum oven overnight at 110 °C before use. Tetraethoxysilane (TEOS) and the diamino-containing silane coupling agent *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane (AEAPS) were purchased from TCI Chemicals. The non-stabilized high density polyethylene (HDPE) powder with the melt flow index of 0.33 g/10min (190 °C, 2.16 kg) was supplied by petrochemical institute, China National Petroleum Corporation. Isopropanol was analytical grade and purchased from Beijing Chemical Works. All the reagents were used as-received without further treatment.

2.2. Preparation of CCS

The co-condensed nanosilica (CCS) was prepared by the co-hydrolysis and co-condensation of TEOS and AEAPS in the mixture of isopropanol and deionized water (Scheme 1). Typically, 83.3 g (0.4 mol) TEOS and 22.2 g (0.1 mol) AEAPS were added into the mixture of 1000 mL isopropanol and 144 mL deionized water. The system was stirred for 6 h to obtain an opaque admixture. The

product was filtered under positive pressure by a polytetrafluoroethylene microfiltration membrane with average pore size of 0.22 μm, and then washed 3 times with ethanol and dried at 60 °C for 12 h.

2.3. Preparation of HDPE composites

The HDPE/CCS composite was prepared by melt blending using a HAAKE PolyLab OS RheoDrive 7 (Themofisher Scientific, Germany) at 200 °C with a screw speed of 50 rpm for 6 min. HDPE/FS composite and HDPE samples were also obtained following the same procedure as reference samples. The content of nanosilica was fixed at 5.0 wt.%. Testing specimens were prepared by hot compression molding at 200 °C. Films with thickness of 45 μm were used for accelerated aging test and disks with thickness of 500 μm for TGA and OIT test.

2.4. Aging tests

Oxidation induction time (OIT) measurement was performed on a Perkin Elmer DSC 7 instrument according to the method provided by ISO 11357-6-2008, which specified the gas flow rate and temperature programming. Firstly, the sample was held at 60 °C for 5 min under a nitrogen flow rate of 50 mL/min. Subsequently, the sample was heated to 200 °C with a heating rate of 20 °C/min, and held for 5 min under the nitrogen flow. Then the gas was switched to oxygen at a flow rate of 50 mL/min and held at 200 °C. The oxidation of the samples was observed as a sharp change in heat flow due to the exothermic nature of the oxidation reaction. The time interval between the switch of gas flow and the intercept point determined by tangent method was determined as OIT.

The accelerated thermo-oxidative aging test of HDPE and HDPE/silica composites was carried out in an aging oven at 100 °C. The accelerated UV degradation test was carried out in a CL-1000 Ultraviolet Crosslinker (UVP LLC) instrument at constant temperature of 40 °C. The wavelength of radiation was 302 nm, and the intensity of the UV light was about 80 000 μW/cm². At appropriate time intervals, the samples were taken out and characterized by IR.

2.5. Characterization methods

Transmission electron microscope (TEM) micrographs were obtained with a JEOL JEM-2200FS instrument with an acceleration voltage of 200 kV.

²⁹Si cross-polarization (CP)-magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectra were recorded with a Bruker Avance III 400 solid-state NMR spectrometer.

X-ray photoelectron spectroscopy (XPS) data was obtained with an ESCALab 220i-XL electron spectrometer from VG Scientific using 300 W Al K_α radiations. The base pressure is about 3 × 10⁻⁹ mbar. The binding energy is calibrated by the C1s line at 284.6 eV from adventitious carbon.

Thermal gravimetric analysis (TGA) was performed on Perkin-Elmer Pyris one in air atmosphere and Perkin-Elmer TGA 8000 in nitrogen atmosphere at a heating rate of 20 °C/min. Isothermal thermal gravimetric analysis (isothermal-TGA) was carried out on Perkin-Elmer Pyris one at 280 °C in air atmosphere.

Scanning electron microscope (SEM) micrographs were taken on a JEOL JSM-6700F field-emission scanning electron microscope with an acceleration voltage of 10 kV. The specimen of SEM was fractured in liquid nitrogen. The fractured surfaces were coated with platinum to enhance the conductivity.

Nitrogen adsorption-desorption isotherms were obtained on Quantachrome NOVA 2200e Surface Area & Pore Size Analyzer at 77 K under continuous adsorption condition.

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