Composites Communications 3 (2017) 51–58

Contents lists available at ScienceDirect

Composites Communications

journal homepage: www.elsevier.com/locate/coco

Photo- and thermo-oxidative aging of polypropylene filled with surface modified fumed nanosilica

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ARTICLE INFO

Keywords:
Fumed nanosilica
Surface modification
Aging
Polypropylene

ABSTRACT

Fumed nanosilica (FS) was treated separately by different silane coupling agents, including *n*-dodecyl-trimethoxyl silane (DTMS), aminoethylaminopropyl-trimethoxyl silane (AEAPS), aminopropyl-trimethoxyl silane (APS) and methacryloxypropyl-trimethoxyl silane (MAPS). Their influences on photo- and thermo-oxidative aging of polypropylene were evaluated by Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). The photoaging of polypropylene was accelerated by the MAPS-modified FS but delayed by the neat FS and other modified FS. On the other hand, the thermal and thermo-oxidative stability of polypropylene were improved with the incorporation of the nanoparticles, independent of the modification. The AEAPS-modified FS and the APS-modified FS revealed simultaneously noticeable enhancement in both photo-stability and thermo-oxidative stability of polypropylene. The possible mechanism was discussed.

1. Introduction

Fumed nanosilica (FS) is a finely divided amorphous silicon dioxide synthesized by high temperature hydrolysis of silicon tetrachloride in oxygen-hydrogen flame [1,2]. It has extremely large specific surface area covered with numerous silanol (Si-OH) groups [3,4] and thus is often used as a versatile additive. With the addition of FS, rubbers and plastics obtain great enhancement in mechanical and thermal properties [5–8], coatings and pigments show better stability and UV resistance [9–11], ceramics get improvement on durability and crack resistance [12,13], cement shows significant enhancement in mechanical properties [14], adhesives get enhanced in thermal, rheological and mechanical properties [11,15–17]. Additionally, FS is odorless, tasteless and thoroughly non-toxic and non-irritating [3,18], so it is also used in cosmetics.

The performances of nanocomposites are largely depending on the uniformity and dispersity of nanoparticles in the matrix. Due to the large specific surface area distributed with abundant silanol groups, FS tend to form aggregates and agglomerates by hydrogen bonding and/or condensation. In consequence, surface modification is necessary to improve its compatibility and its dispersity with the matrix. Silane coupling agents are most commonly used surface modifiers, which could not only enhance the dispersity but also further improve the mechanical, thermal and optical properties of the matrix [6,8,19–24].

Polypropylene (PP) is one of the most widely used commercial thermoplastic. It has been reported that when filled with FS, the tensile strength, modulus, thermal stability and flame retardant property of PP was enhanced and the gas permeability was weakened [3,25–31]. It has been found that when modified with different silane coupling agents, the effect of nanosilica on the thermal and mechanical properties of polymer varies [6,19,23,24,32].

Due to the existence of abundant hydrogen of the tertiary carbon atom, PP is vulnerable to photo- and thermo-oxidative degradation [33,34]. However, the influences of FS surface treatment on the degradation of PP have not yet received adequate attention in available studies. In this work, FS was treated with different silane coupling agents and compounded with PP. The influences of the FS modification on photo- and thermo-oxidative degradation have been evaluated.

2. Results and discussion

2.1. Characterization of FS treated with silane coupling agents

FS was treated with *n*-dodecyl-trimethoxyl silane (DTMS), ami-

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http://dx.doi.org/10.1016/j.coco.2017.02.004
Received 19 October 2016; Received in revised form 16 February 2017; Accepted 16 February 2017
Available online 23 February 2017

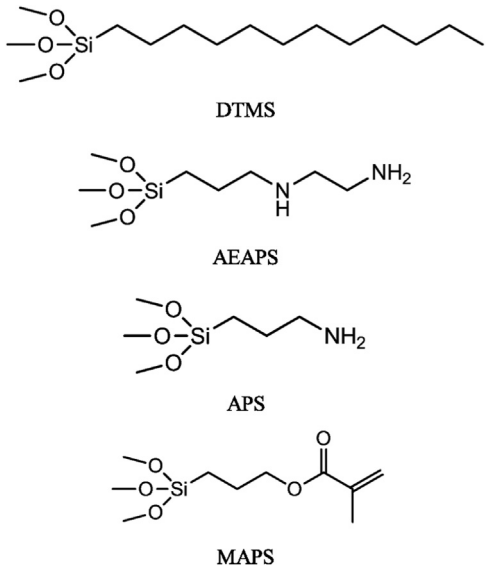

Fig. 1. Chemical structures of various silane coupling agents.

noethylaminopropyl-trimethoxyl silane (AEAPS), aminopropyl-trimethoxyl silane (APS) and methacryloxypropyl-trimethoxyl silane (MAPS) separately. The chemical structures of these silane coupling agents are shown in Fig. 1.

The surface chemistry of the neat FS and the modified FS was studied by FTIR as showed in Fig. 2. The broad strong bands around 3100–3700 cm^{-1} are assigned to the O-H stretching vibration of silanol hydroxyls and adsorbed water, while the absorption at 1630 cm^{-1} is assigned to the O-H bending of adsorbed water. In the DTMS-modified FS (DTMS-FS), the bands around 2929 cm^{-1} and 2858 cm^{-1} are attributed to CH_2 asymmetric and symmetric stretches, respectively, while the absorption at 1462 cm^{-1} is characteristic of CH_2 bending. In the AEAPS-modified FS (AEAPS-FS) and the APS-modified FS (APS-FS), the absorption of N-H bending at 1570 cm^{-1} is noticeable and a weak signal of CH_2 stretching vibration at around 2940 cm^{-1} is detected, which indicate the successful modification of FS with AEAPS and APS. For the MAPS-modified FS (MAPS-FS), the absorption at 1710 cm^{-1} corresponds to the stretching vibration of carbonyl group. The absorption bands around 2940 cm^{-1} and 2870 cm^{-1} are attributed to CH_2 asymmetric and symmetric stretches. The FTIR results confirmed that the silane coupling agents were successfully grafted on the FS nanoparticles.

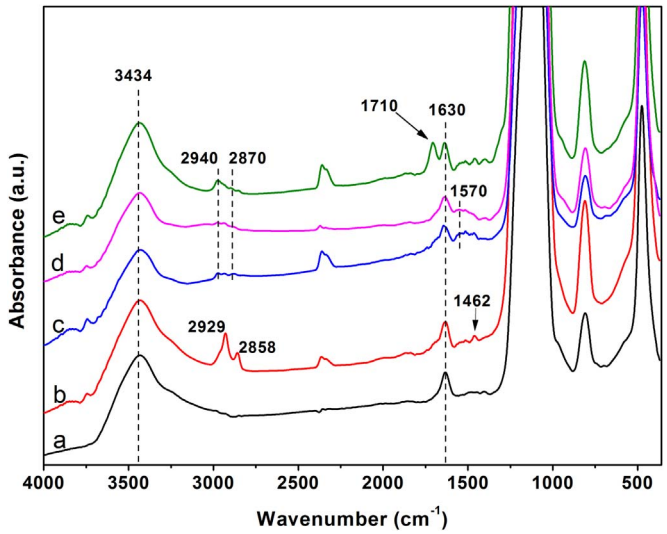

Fig. 2. FTIR spectra of (a) FS, (b) DTMS-FS, (c) AEAPS-FS, (d) APS-FS, (e) MAPS-FS.

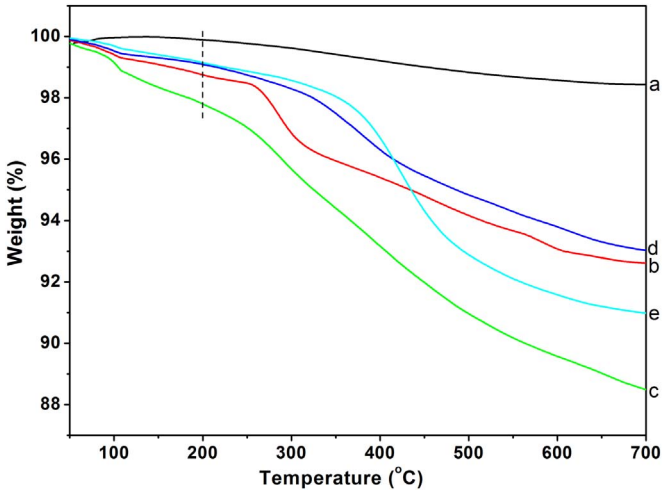

Fig. 3. TGA curves of (a) neat FS, (b) DTMS-FS, (c) AEAPS-FS, (d) APS-FS, (e) MAPS-FS in nitrogen atmosphere.

Table 1.
Organic content of silane modified FS based on TGA results.

Sample ID	Weight at 200 °C (wt %)	Weight at 700 °C (wt %)	Delta weight (wt %)
DTMS-FS	98.7	92.6	6.1
AEAPS-FS	97.8	88.5	9.3
APS-FS	99.1	92.9	6.2
MAPS-FS	99.2	91.0	8.2

The TGA results of the neat FS and the modified FS in nitrogen atmosphere are presented in Fig. 3. Based on the weight losses from 200 °C to 750 °C, the organic content of each modified FS was calculated and listed in Table 1. The content of organic part in the modified FS ranged from 6.1 wt% to 9.2 wt%.

2.2. Dispersion of the nanoparticles in PP/silica nanocomposites

PP/silica nanocomposites were prepared by melt blending with formulations listed in Table 2. The inorganic content of each composite is fixed at 4.0 wt%. The prepared materials were hot-pressed into films with an average thickness of 40 μm for the aging tests.

The dispersion states of the neat FS and the modified FS in the PP/silica nanocomposites was characterized by SEM as shown in Fig. 4. The neat FS was poorly dispersed in the PP matrix as large aggregates and agglomerates observed (Fig. 4**a**). DTMS-FS and MAPS-FS were uniformly dispersed in the PP matrix (Fig. 4**b** and **e**) due to the improved affinity between PP and the organic group on the surface of modified nanosilica. The AEAPS- and APS-modified FS also promoted the dispersion of nanosilica in the PP matrix (Fig. 4**c** and **d**), but there were still a few aggregations, which is probably because of strong polarity of the amino groups on the nanoparticles.

Table 2.
The formulations of PP and PP/silica nanocomposites.

Sample ID	Type of additives	Content of additives (wt%)
Pure PP	/	/
PP/FS	Neat FS	4.00
PP/DTMS-FS	DTMS-FS	4.32
PP/AEAPS-FS	AEAPS-FS	4.54
PP/APS-FS	APS-FS	4.32
PP/MAPS-FS	MAPS-FS	4.40