Short communication

A facile strategy for functionalizing silica nanoparticles by polycarbonate degradation and its application in polymer nanocomposites

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ABSTRACT

The degraded polycarbonate (PC) chains were successfully grafted onto the surface of silica nanoparticles (nano-SiO_2) by melt blending. Covalent linkage (Si−O−C bond) was formed between the degraded PC chains and nano-SiO_2 under the condition of strong shear force and high temperature. The alcoholysis between carbonate and Si−OH groups, coupled with the condensation reaction between silicon hydroxyls and hydroxyl end groups of degraded chains, mainly contributed to the formation of Si−O−C bond. As expected, the tensile strength and toughness of PC were simultaneously enhanced by incorporating functionalized SiO_2. The improvement in tensile properties was attributed to the strong interfacial adhesion between functionalized SiO_2 and PC matrix.

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1. Introduction

Remarkable improvement in physical properties of polymers is theoretically expected when adding a small amount of SiO_2 nanoparticles due to enormous specific surface area of nano-SiO_2. Unfortunately, the agglomeration of nanoparticles and the poor interfacial interaction between nanoparticle and matrix result in that the actual values of physical properties are far less than the theoretical values [1]. Accordingly, most researchers in this field focus their attention on the surface modification of nano-SiO_2, such as grafting surfactant [2] or polymer [3]. However, the disadvantages of the above-mentioned approaches including complicated process, high cost and low efficiency, make them unsuitable for mass production of polymer nanocomposites.

Recent studies showed that the interface properties of aromatic polymer/carbon nanotube or graphene composites can be enhanced by simple melt blending due to the formation of π−π interaction [4−6]. However, the mechanical properties of the above composites deteriorate due to the serious degradation of polymer [5]. For polycarbonate (PC), its degradation during melt blending

with inorganic nanoparticles is particularly outstanding and inevitable [7,8]. Our previous study also reported that the surface hydroxyls of nano-SiO_2 can accelerate the pyrolysis of PC by reacting with carbonate groups [9]. For nanoparticle-reinforced polymers, the contradiction between long-time melt processing for obtaining strong interfacial interaction and polymer degradation is nearly irreconcilable. Even so, it should be noted that a flexible interface on the surface of nanoparticles is formed via melt blending. Herein, an idea that if the flexible interface can be employed to functionalize nanoparticles arises. If feasible, the functionalized nanoparticles can be further used as filler to improve the properties of polymers.

In this work, the interfacial interaction between nano-SiO_2 and PC matrix during melt blending was confirmed and utilized to functionalize SiO_2. Compared with traditional chemical modification, our method for functionalizing SiO_2 are simple, effective and low-cost. Moreover, the functionalized SiO_2 was introduced into PC matrix to explore its application in polymer nanocomposites.

2. Experimental

Functionalized SiO_2 was prepared via reactive melt blending with PC (detailed description is schematically shown by Fig. S1 in

Supplementary data). Briefly, PC (Wonderlite PC-110) and 10 wt% fumed SiO_2 (250 ± 30 m^2/g) were firstly pre-mixed by solution blending in tetrahydrofuran (THF) to obtain Mixture-1. The dried Mixture-1 was subsequently melt mixed for 10 min to produce Mixture-2 by using a twin-screw micro-extruder (SJZS-10, China) with a melt temperature of 250 °C and a screw speed of 30 rpm. After that, the nanoparticles in Mixture-1 (abbr. SiO_2-0) and Mixture-2 (i.e., PC-functionalized SiO_2, abbr. SiO_2-10) were extracted by a dissolution, centrifugation, washing and drying process.

PC composites with 1 wt% pristine SiO_2 (abbr. PCSp) and SiO_2-10 (abbr. PCS10) were prepared through solution mixing. Tensile samples were fabricated by hot compression molding at 240 °C and 15 MPa. Neat PC sample as a reference was prepared in the same way. The drying process at 80 °C for 24 h in vacuum was employed for all of the raw materials mentioned above.

Fourier transform infrared spectra (FTIR, transmission-mode) were recorded in the wavenumber range of 650–4000 cm^{-1} using a Nicolet 6700 FTIR spectrometer with a spectral resolution of 2 cm^{-1}. X-ray photoelectron spectroscopy (XPS) was carried out on a Thermo ESCALAB 250Xi spectrometer using an Al Kα exciting radiation. Thermogravimetric analyses (TGA) were conducted on a Mettler-Toledo TGA/DSC 1 analyzer with a heating rate of 20 °C/min under nitrogen protection. The morphology of nanoparticles was observed by a Tecnai G2 20 S-TWIN transmission electron microscope (TEM). Static contact angles of nanoparticles with double-distilled water were measured with a contact angle goniometer (JC2000C) at room temperature. Tensile testing was performed by using a SUNS UTM2203 universal tensile testing machine at a crosshead rate of 10 mm/min. The tensile fracture surfaces of PCSp and PCS10 were sputter-coated with gold and observed with a JEOL JSM-7500F field emission scanning electron microscope (FE-SEM).

3. Results and discussion

3.1. Characteristics of PC-functionalized SiO_2

Organic coating of SiO_2 can be easily detected and quantified by means of TGA measurement. Fig. 1a shows the TGA curves of various SiO_2 and neat PC. Both pristine SiO_2 and SiO_2-0 exhibit an inconspicuous mass loss (ca. 2.3%) within the testing temperature range, indicating that no PC chain is attached after solution mixing. However, an obvious mass loss is observed for SiO_2-10 in the temperature range of 350–550 °C which is lower than the decomposition temperature of neat PC, suggesting that degraded PC chains are attached onto SiO_2-10 during melt blending. Considering that pristine SiO_2 and neat PC lose 2.3% and 73.1% of their original weight, the coated PC content of SiO_2-10 is calculated to be 30.2%.

The covalent bonds linking SiO_2 and PC chains were detected by FTIR and XPS technologies. Fig. 1b illustrates the FTIR spectra of pristine SiO_2, SiO_2-10 and neat PC. In contrast to pristine SiO_2, some new absorption peaks which belong to PC, including C–H stretching vibrations at 2972, 2876 cm^{-1}, C=O stretching vibration at 1779 cm^{-1}, skeletal vibration of phenyl at 1510 cm^{-1} and C–O–C stretching vibrations at 1226, 1196, 1164 cm^{-1}, are found in the SiO_2-10 spectrum, and the Si–OH peak at 3440 cm^{-1} for SiO_2-10 weakens greatly. These results indicate that PC chains are grafted onto the surface of SiO_2 by reacting with Si–OH groups. Besides, the blue shift of C=O infrared peak of SiO_2-10 relative to neat PC (Fig. 1c) suggests that alcoholysis reaction occurs between Si–OH and carbonate groups as Schematic I in Fig. 2, which will be discussed in the next section. Herein, a (C=O)–O–Si group is proposed to link nano-SiO_2 and degraded PC chains [10].

The suggested (C=O)–O–Si group was further verified by XPS measurement. The XPS spectra of pristine SiO_2, SiO_2-10 and neat PC and various fitting peaks corresponding to the chemical groups in C 1s and Si 2p XPS regions are shown in Fig. 1d–f, respectively. The carbon peak (Fig. 1d) and the new groups in C 1s region (Fig. 1e) including phenyl, C–O–C, and C=O, arise in the SiO_2-10 spectrum, reconfirming the PC coating. Moreover, the shifts of the fitting peaks of C–O–C and C=O groups compared with neat PC suggest the existence of (C=O)–O–Si group. In Si 2p region (Fig. 1f), four fitting peaks located at 100.6, 101.2, 103.7 and 105.5 eV, which are respectively attributed to Si–O_1, Si–O_2, Si–O_4 and Si–OH, are observed for pristine SiO_2. However, only the main peak (103.7 eV)
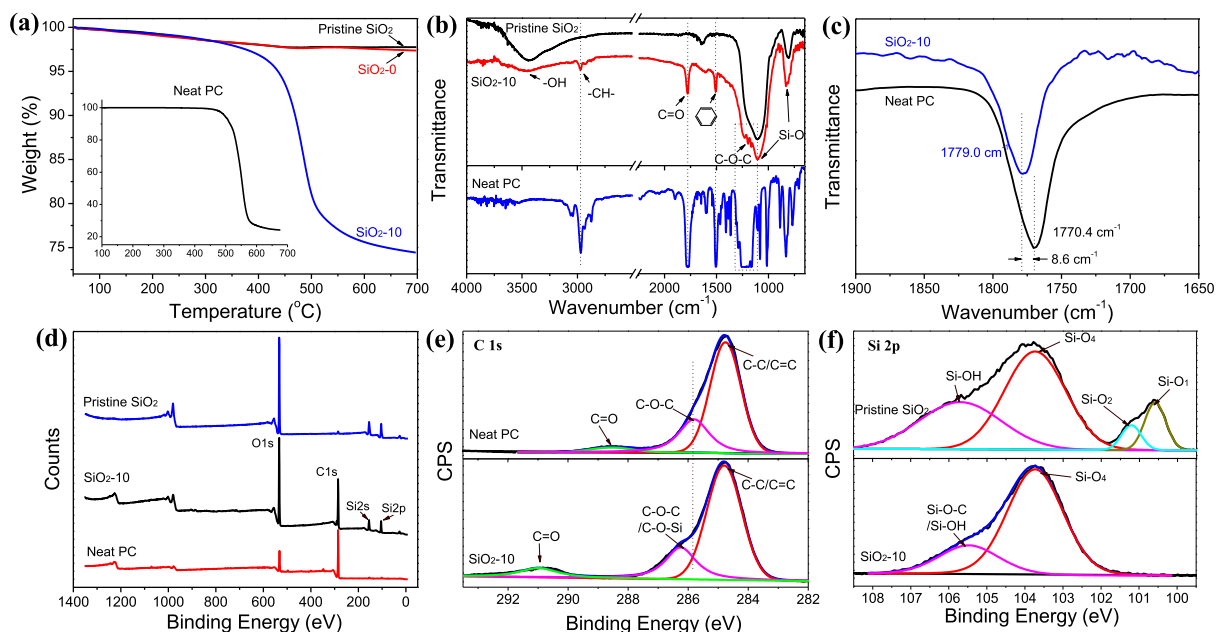

Fig. 1. (a) TGA curves of various nano-SiO_2 and neat PC (inset); (b) FTIR and (d) XPS spectra of pristine SiO_2, SiO_2-10 and neat PC; (c) FTIR spectra of neat PC and SiO_2-10 in C=O stretching region; (e, f) High resolution XPS spectra of C 1s and Si 2p regions.