Research paper

Experimental analysis of stabilizing effects of carbon nanotubes (CNTs) on thermal oxidation of poly(ethylene glycol)–CNT composites

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ABSTRACT

In this work, the thermal stabilization of poly(ethylene glycol) (PEG) by super-growth carbon nanotubes (SGCNTs) is studied by analyzing degraded compounds via high-resolution matrix-assisted laser diffusion ionization time-of-flight mass spectroscopy and IR techniques. SGCNTs successfully suppress the thermal oxidation of PEG, and the components of the degraded compounds change upon addition of SGCNTs to PEG. The SGCNTs quench mainly the RO radical generated by the initial chain scission of the C—O bond of PEG, resulting in the suppression of the intermolecular proton abstraction.

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1. Introduction

Owing to their strength, electron conductivity, and thermal conductivity, carbon nanotubes (CNTs) have attracted increasing attention as future nanomaterials [1–3]. As CNTs can be also used as fillers to improve the properties of polymers, many polymer–CNT composites have been developed [3–5]. In particular, thermal stabilization of polymers is one of the most attractive benefits of CNTs; CNTs stabilize polypropylene [6,7], polyethylene [6,8,9], and polycarbonate [10]. The stabilization mechanisms have been discussed in several reports. For example, Hsu's research group suggested that 'acceptor-like localized states' (vacancies, dangling bonds, OH and CO substrates) work as radical scavengers [6]. Wang and co-workers reported that OH radical scavenger properties for suspensions in solutions, measured by spin-trap electron spin resonance technique, and defect concentration of CNTs, estimated by Raman spectroscopy, were related to the thermal stability of high-density polyethylene–CNT composites [8]. Thus, CNTs can stabilize various polymers, owing to their radical trapping properties [7,9,11]. However, the radical species preferentially quenched by CNTs during thermal oxidation of polymer–CNT composites have not been clarified yet. As several kinds of radicals (e.g., R, RO, ROO, and OH) are generated during the thermal oxidation of a

polymer [12,13], model experiments analyzing a single radical component may not be reliable to examine the effects of CNTs.

In this work, we examined the effects of CNTs on the thermal oxidation of a polymer–CNT composite by performing a detailed experimental analysis focusing on the degraded compounds originated from the polymer–CNT composite, instead of model solutions. Here, we used poly(ethylene glycol) (PEG) and super-growth CNTs (SGCNTs) to prepare the polymer–CNT composite, and examined the differences in thermal degraded compounds of PEG and the PEG–SGCNT composite. As PEG is easily oxidized and results almost completely in the formation of soluble liquids or gas compounds [14–20], a quantitative analysis could be performed [14,20]. SGCNTs are synthesized by water-assisted chemical vapor deposition in our research group in 2004 [21–23]. We adopted them in this study since their purity is quite high thus we can examine the effects of only CNTs, excluding those of metal impurities working as a catalyst on the polymer degradation. As described above, once the radical species preferentially quenched by CNTs are clarified, material design for further stabilization could be directed by the obtained results.

2. Experimental

2.1. Fabrication of PEG–SGCNT composite (PEG-SGCNT)

SGCNTs [21] (>99.98% in purity, >1 mm in length, 3 nm in diameter) were used unless otherwise specified. SGCNTs were added to

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chloroform and processed for 24 h by using an ultrasonic homogenizer (130 W, 20 kHz, Vibra-Cell VCX130, Sonics). Afterwards, PEG (Mw = 300,000–500,000, Wako) was added to the SGCNT/chloroform solution to form PEG-SGCNT in a weight ratio of 99:1. The mixture was stirred at 40 °C for 24 h to remove the solvent; the resulting gel-like solution was poured onto a glass plate by drop casting, and then air-dried for 24 h to obtain PEG-SGCNT.

2.2. Thermal oxidative degradation

Thermogravimetric (TG) measurements of PEG and PEG-SGCNT by using a TG/DTA6200 (Hitachi High-Tech Science Corporation). The thermal oxidative degradation of PEG-SGCNT was performed using a heat chamber (volume = 25 mL) at 473 ± 0.5 K (type-900, S.T. Japan Inc., Japan), attached to a long-path IR cell (optic path = 10 m, volume = 2000 mL) (S.T. Japan Inc., Japan) equipped with a Fourier transform IR spectrometer (Nicolet iS50, Thermo Scientific, US; 0.5 cm^{-1}; MCT).

2.3. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS)

A 2,5-dihydroxybenzoic acid (DHB) matrix was dissolved in tetrahydrofuran (THF) at a concentration of 10 mg/mL. 5 μL of the matrix solution were added to the 1 μL of a THF solution of the thermally degraded PEG-SGCNT (10 mg/mL). Finally a solution of sodium trifluoroacetate in THF was added to the mixture. After the 1 μL of solution was casted and dried on the target plate (Hudson Surface Technology Inc., Old Tappan, USA), MALDI-TOF mass spectra were recorded using a JMS-S3000 MALDI spiral TOF MS (JEOL, Akishima, Japan) with a flight length of ca. 17 m and eight cycles of the spiral trajectory to achieve a high mass-resolving power. Ions generated by irradiation with a 349-nm Nd:YLF laser were accelerated at 20 kV. The delay time and grid voltage were optimized to maintain M < ca. 0.03 Da at the FWHM over the observed mass range. Mass calibration was made using a PEG standard as an external standard. To obtain the highly calibrated m/z, unchanged PEG in the degraded PEG-SGCNT was employed for an internal standard. Relative yield of each degraded compound was estimated as its relative intensity of isotopic peak to the sum of all isotopic peaks from compounds listed in Table S1.

3. Results and discussion

3.1. Thermal stabilization of PEG by SGCNTs

The SGCNT stabilization effect on PEG was estimated by TG measurements of PEG and PEG-SGCNT. The results of the heating at 10 K min^{-1} are summarized in Table 1, and the TG curves are shown in Fig. S1 (see Supplementary Information). PEG showed 5% weight loss at 229 °C (T_{95}) and 90% weight loss at 363 °C (T_{10}); PEG-SGCNT showed a similar T_{95} value, but a considerably higher T_{10} value of >400 °C. The results indicated that the SGCNTs suppressed the thermal oxidative degradation of PEG. To examine further differences between PEG and PEG-SGCNT, the weight losses were measured under isothermal conditions at 200 °C after heating from 30 to 200 °C at 10 K min^{-1} (Fig. 1). During the heating process, both materials showed almost no weight loss. However, during isothermal heating at 200 °C, PEG rapidly degraded, whereas PEG-SGCNT degraded slowly. After reaching 200 °C, PEG showed 90% weight loss after 28 min, while a period of 345 min was necessary for PEG-SGCNT to reduce its weight to 10%.

Based on the two kinds of measurements, SGCNT reduced the thermal degradation rate, but it did not improve the degradation starting temperature. This result shows that SGCNT suppresses the radical reactions, but does not impact thermal decomposition. The stabilization properties were similar to those of other CNTs [6–8,10]; thus, we expected that the experimental study on thermal degradation of PEG-SGCNT provides the details of the radical reactions suppressed by CNTs.

3.2. Effects of SGCNTs on thermal oxidation of PEG

During the thermal oxidation of PEG, R·, RO·, ROO·, OH· are formed as radical species [14–20]. As shown in Fig. S2, R· radicals are formed by the thermal chain scission of C—O, proton abstraction by OH·, and β-scission of RO·. The RO· radicals originate from the thermal chain scission of C—O or decomposition of ROOH, which also generates OH·. ROO· is derived by O$_2$ adduction to R·. The presence of SGCNTs affects the generation or consumption of these radicals, and it also changes the amounts or compositions of the degraded compounds.

We first focused on the relationships between radical species and degraded compounds since we can concern the degraded compound but it is difficult to observe radicals in polymers. Therefore, we examined sequential reactions from PEG to degraded compounds as shown in Scheme 1. The thermal chain scission results in the formation of ethyl radical **H—CH$_2$CH$_2$·** and alkoxy radical **H—O·**. **H—CH$_2$CH$_2$·** reacts with O$_2$ and converts to **H—OO·**. Further reactions of the two peroxide radicals result in two **H—O·** radicals or **H—CHO** and **H—H**. The simulated rate constants of the former and latter reactions were 2.76 × 10^{-13} and 1.4 × 10^{-14} cm^3 molecule^{-1} s^{-1}, respectively [20]. As the former reaction is over 10 times faster than the latter, the formation of **H—CHO** and **H—H** from the two peroxide radicals was omitted in this study. When O$_2$ reacts with **H—O·**, methylene formyl termination is generated, resulting in **H—CH$_2$CHO**. Further reaction with OH·
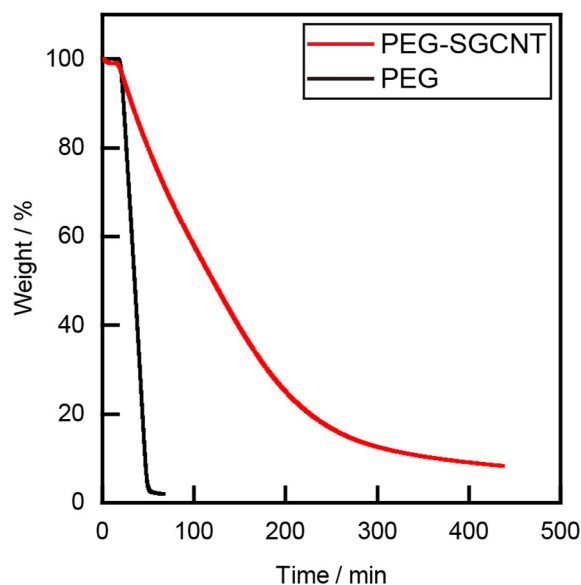

Fig. 1. Weight losses of poly(ethylene glycol) (PEG; black) and PEG–super-growth carbon nanotube composite (red) after heating from 30 to 200 °C at 10 K min^{-1}, followed by isothermal heating at 200 °C. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
Thermogravimetric analysis of PEG and PEG-SGCNT.

Material	T_{95} [°C]	T_{10} [°C]
PEG-SGCNT	235	>400
PEG	229	363