Electron microscopic studies on disintegration of core/shell polymer structure during heat treatment process in carbon nanotube preparation by polymer blend technique

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The polymer blend technique has been revealed to give a poor yield in the preparation of carbon nanotubes (CNTs) by spinning three-layered core/shell polymer particles having different thermal decomposition properties. In order to elucidate the reason for the low yields obtained by this method, we carried out the present study on employing three-layered core/shell particles, (core) PMMA / PAN-PMAA / PMMA (shell), with electron microscopic techniques. The core/shell structure was not disintegrated by the stabilization and carbonization processes. The influences of the copolymer composition of the carbon precursor polymer (CPP), PAN-PMAA, on the deformation of the core/shell structures were studied. When the concentration of PMAA in the PAN-PMAA copolymer is 3 mol %, the core/shell structure was retained, but when the concentration of PMAA was increased to 7.5 mol %, the core/shell structure disintegrated. By using a copolymer with 4 mol % PMAA, a hollow cigar-like nanostructured carbon was formed; this can be considered to be an indication for the formation of a CNT. Thus, the copolymer composition was found to be an important parameter for the preparation of CNTs by the polymer blend technique. The results obtained in this study indicated the possibility of obtaining CNTs by properly tuning the copolymer composition of the CPP.

KEYWORDS : Nano-structured carbon, Heat treatment, Transmission electron microscopy

1. Introduction

Carbon nanotubes (CNTs)¹⁾ have attracted the attention of researchers to a considerable extent owing to their peculiar structures and possible applications in various fields, such as electronics, and also as nanocomposites and catalyst supports. These materials have been prepared by arc discharge²⁾, laser ablation^{3), 4)}, catalytic CVD (CCVD)⁵⁾, and template methods⁶⁾. The CCVD method is recognized as the most successful industrial method for the production of multiwalled CNTs. The CNTs prepared by this method usually contain metal particles used as catalysts inside their bodies; the removal of these metal particles is required for enhancing the practical applicability of the CNTs⁷⁾⁻⁹⁾. Further purification of these CNTs requires additional costs; hence, an alternative method is required for the preparation of CNTs without metal species.

The polymer-blend method, which was invented by Oya's group, has been revealed to be a useful method for the construction of

nanostructured carbon materials¹⁰⁾. The basic idea of this method is to combine several polymers exhibiting different behaviors during their thermal decomposition. Kasahara and Oya showed the preparation of carbon nanofibers by this method¹⁰⁾. Further, Patel and Oya successfully constructed nanostructured carbons by this method, such as lotus-type porous carbon fibers, *i.e.*, a bundle of carbon nanofibers surrounded by a thin carbon sheath¹¹⁾.

Oya *et al.* have attempted to apply this idea to produce carbon nanotubes by the procedure shown in **Fig.1**. The essence of the method is to elongate a three-layered core/shell particle, where the core, inner shell, and outer shell are composed of polymers with different thermal properties; *i.e.*, the core and the outer shell are composed of thermally decomposable polymers (TDP), while the inner shell is composed of polymers that yield carbonaceous residues (carbon precursor polymers, CPP). If the inner shells are successfully stabilized, successive carbonizations will lead to the formation of CNTs. Since this method does not require metal catalysts

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(Received October 8, 2008, Accepted January 9, 2009)

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Fig.1 Scheme of the polymer blend technique for preparing CNTs. Two different types of polymers are used for this preparation: a thermally decomposable polymer (TDP) and a carbon precursor polymer (CPP). The three-layered core/shell particles are elongated by spinning followed by stabilization of CPP in the second layer and carbonization. During the carbonization process, both the TDP phases decompose to leave behind hollow tubular carbons.

to construct nanostructures, the CNTs thus prepared will be completely liberated from the purification process. However, the yield of the CNTs by this method is very low.

Previously, we speculated the disintegration of the core/shell structures, which was caused by heating during the spinning process, as the principal reason for the low CNT yields. We invented a high-speed centrifugal spinning apparatus¹²⁾ in order to shorten the time spent by the polymers at elevated temperatures in the melting pot of the spinning apparatus. This apparatus enabled us to prepare CNTs with yields higher than those obtained by the conventional method when a PAN-PS copolymer was employed as the CPP constituent, where PAN and PS stand for polyacrylonitrile and polystyrene, respectively. However, the details of the disintegration process and the factor that led to the disintegration have not yet been clarified.

In the present study, we conducted studies to study the details of the disintegration of the core/shell structure by observing each step of the preparation procedure, *i.e.*, the spinning, stabilization, and carbonization processes, by detailed electron microscopic techniques and to understand the factor that led to the disintegration.

2. Experimental

2.1 Preparation of three-layered core/shell structure

Three-layered core/shell particles were prepared by a three-step preparation method: (1) formation of core-particles by soap-free polymerization, (2) formation of a CPP layer onto the core particle by starvation polymerization, and (3) covering the product particles obtained in step (2) with TDP. $K_2S_2O_8$ was employed as the initiator for the polymerization reactions in the present study, which was supplied as an aqueous solution of a concentration of 2 mg/g in terms of the mass ratio of $K_2S_2O_8$ /distilled water.

Step 1: Poly (methyl methacrylate) (PMMA) was employed as the constituent for the core particles. After adding methyl methacrylate (MMA 35 g) and distilled water (300 g) into a four-necked flask, the air in the flask was purged by flowing N_2

gas for 20 min along with stirring using a propeller at 75 rpm. The polymerization reaction was initiated by adding 50 g of the $K_2S_2O_8$ solution, and was continued for 4 h with stirring at 300 rpm. The product was obtained as a suspension.

Step 2: The starvation polymerization of AN and MAA was performed by the dropwise addition of a mixture of acrylonitrile (AN) and methacrylic acid (MAA) (3.6 g/0.2 g) into a solution containing the abovementioned suspension (45 g of the suspension and 50 g of the $K_2S_2O_8$ solution) at the rate of 0.2 ml/min. The polymerization was continued for 2 h at 65 °C with stirring at 300 rpm in a nitrogen-substituted flask.

Step 3: The outer PMMA layer was formed onto the core-shell particles prepared in Step 2 by the dropwise addition of 7.7 g of MMA to the suspension containing 50 g of the $K_2S_2O_8$ solution at the rate of 0.4 ml/min. The reaction temperature was 65 °C. After the polymerization, the particles were retrieved by centrifugation at 5000 rpm and drying at 65 °C overnight. The purpose of introducing the third layer was to prevent the adhesion of the PAN-PMMA copolymer during the heat-treatment process. Several other three-layered core/shell particles with different inner layer constituents were also prepared in the same manner. Hereafter, the three layered core-shell particles will be referred to as xPMAA, where “x” is the copolymer ratio (3, 4, or 7.5) and PMAA is the component of the inner shell.

2.2 Spinning

4PMAA and 7.5PMAA were spun in the high-speed centrifugal spinning apparatus¹³⁾. The spinning temperature was varied depending on the polymers to be spun: 260 °C for 4PMAA, and 260 °C and 200 °C for 7.5PMAA. The rotation speed was fixed at 5000 rpm.

2.3 Stabilization and carbonization

The obtained fibers were subjected to a stabilization process in order to avoid melting during the course of carbonization. This was performed by heating the fiber in an electric furnace in the following manner; holding at 220 °C for 3 h in an air stream by using the heating rate of 5 °C/min (< 150 °C) and 1 °C/min (> 150 °C). The stabilized fiber was then carbonized at 1000 °C for 10 min in a N_2 stream at a heating rate of 5 °C/min.

2.4 Characterization

The structures of the core-shell polymers and their carbonized samples were examined by TEM (JEM-2010, JEOL) and FE-SEM (JSM-6700FS, JEOL). A study on the thermal disintegration of the core/shell structures was conducted for 3PMAA and 7.5PMAA by using TEM coupled with ultra-microtome slicing. Each three-layered core/shell was first heat-treated in a N_2 flow at a preset temperature range between 150 and 390 °C at a rate of 30 °C/min for 1 min, and then embedded in an epoxy resin (Epok 812, Okenshoji Co., Ltd). The embedded sample was sliced into 60-nm-thick pieces by using an ultra-microtome apparatus (Reichert, Supernova)

equipped with a diamond knife. The pieces were transferred to a TEM grid and electron-stained by exposure to OsO₄ vapors for one day.

3. Results and discussion

3.1 Stabilization and carbonization steps

Stabilization is a vital process in the production of carbon fibers; it introduces cross-links between the polymer molecular chains in the fibers by a certain oxidation reaction in order to prevent them from melting during carbonization.

Herein, we conducted a study to verify whether the stabilization and carbonization steps induce the transformation of the layered core/shell structure, which prevents the formation of CNTs. The as-prepared 7.5PMAA particles were subjected to stabilization followed by carbonization. **Fig.2** shows the carbonized polymers. The FE-SEM image shown in **Fig.2** (a) clearly reveals a granular appearance, indicating that no deformation of the particles occurred during the stabilization and carbonization processes. The TEM image shown in **Fig.2** (b) confirms the hollow structure of the obtained material. The results obtained here confirmed that core/shell structures are not disintegrated in the stabilization or

carbonization steps but in the spinning step.

3.2 Deformation in the spinning process

Fig.3 shows the TEM images of the sliced 3PMAA (a-c) and 7.5PMAA (d-f). **Fig.3** (a) and (d) show the initial states of 3PMAA and 7.5PMAA, respectively. Although all the constituents of the core/shell particles are stained by OsO₄, the expected three-layered core/shell structure could be successfully discriminated, as shown in **Fig.3**, where the three different portions are indicated by arrows. The stained portion outside the particle boundary was due to the epoxy resin matrix. From these images, the diameters of the as-prepared particles and the thickness of the inner shells were found to be approximately 300 nm and 40 nm, respectively.

In the case of 3PMAA, as shown in **Fig.3** (a)-(c), the layered structure was maintained when the material was heated at 230 °C (c). On the other hand, 7.5PMAA showed disintegration of the layered structure when heat-treated at 200 °C. From the contrast, the small black spots found in **Fig.3** (e) and (f) were inferred to be due to the PAN-PMAA copolymer. In a preliminary study, it was observed that the spinnability of the PAN-PMAA copolymer depended on its composition; the higher the MAA content in the PAN-PMAA copolymer, the higher its spinnability. This observation indicated the melting or spinning temperature was of the PAN-PMAA copolymer was lowered by the increase in the MAA content. Hence the inner shell made of such copolymers gave rise to less rigid structure, resulting in the disintegration of the core/shell structure by heat-treatment in inert atmospheres. Thus, one of the factors that determined the stability of the layered structure was concluded to be the copolymer composition; *i.e.*, a low MAA content in the PAN-PMAA copolymer would be desirable.

The core/shell particles, 4PMAA and 7.5PMAA, were subjected to spinning, stabilization, and carbonization treatments. The electron micrographs of the carbonized samples are presented in **Fig.4**.

Fig.2 (a) FE-SEM and (b) TEM images of the stabilized and carbonized three-layered core/shell particles, 7.5PMAA. The granular appearance was maintained and formation of hollow particles was observed.

Fig.3 Thermal behaviors of the three-layered core/shell particles having different copolymer compositions of their inner layers. (a) as-prepared 3PMAA; (b) 3PMAA heated at 200 °C; (c) 3PMAA heated at 260 °C; (d) as prepared 7.5PMAA; (e) 7.5PMAA heated at 200 °C and (f) 7.5PMAA heated at 260 °C.

Fig.4 Electron micrographs of the carbonized spun three-layered particles. (a), (b): FE-SEM and TEM images of 4PMAA; (c)-(e): FE-SEM, TEM, and the cross-sectional images of the carbons from 7.5PMAA spun at 260 °C; (f)-(h): FE-SEM, TEM, and cross-sectional images of the carbons from 7.5PMAA spun at 200 °C.

When PAN-co-4 mol % PMAA was used as the constituent of the inner layer; *i.e.*, 4PMAA, peculiarly structured carbons were obtained; *i.e.*, hollow cigar-like structures, the diameter and the length of which were approximately 50 ~ 100 nm and 1 μ m, respectively. Since the formation of such cigar-like structures appeared to be due to the low spinnability of the CPP, we expected to produce more elongated CNTs by employing a CPP polymer with high spinnability, *i. e.* with higher MAA contents.

The results obtained for the CPP with higher spinnability, 7.5PMAA, are shown in **Fig.4** (c)-(h). When the spinning temperature was 260 °C, which is the same as that for 4PMAA shown in **Fig.4** (a)-(b), very thick fibers were obtained, with diameters in the range of approximately 0.1 ~ 1 μ m, as shown in **Fig.4** (c) and (d). In order to observe the effect of lowering the spinning temperature, some polymer was subjected to spinning at 200 °C. As can be seen in **Fig.4** (f) and (g), the reduction in the spinning temperature did not lead to the formation of thin fibers. The formation of thick fibers is rather unusual since we expect the formation of thin carbon fibers if the spinning process had simply elongated the core-shell particles. **Fig.4** (e) and (h) show the cross-sections of the spun fibers spun at 260 °C and 200 °C, respectively. The diameters of the

obtained fibers are in the range of 100 ~ 1000 nm; these diameters are considerably larger than those of the layered core/shell particles shown in **Fig.2**. From these observations, it can be said that the formation of such thick fibers is due to the aggregation of the CPPs during the heat treatment. It should be noted that there are no holes in the cross-section of the fibers, which indicates the complete disintegration of the layered core/shell structures composed with 7.5PMAA as the inner shell constituent.

4. Conclusion

In conclusion, the present study revealed that the most important factor for the formation of CNTs is the thermal stability of CPP, which can be attained by lowering the MAA content in PAN-PMAA copolymers; however, this decrease led to a lower spinnability of the co-polymer. A complete adjustment of the copolymer composition is the key to prepare the CNTs successfully, it would lie in the composition range between 4 ~ 7.5 mol % in the case of PAN-PMAA copolymer. The spinning step, and not the stabilization or carbonization step, has the maximum influence on the heat-treatment process. A careful tuning of the copolymer composition and a proper selection of polymers is the key to the preparation of CNTs by the polymer blend technique.

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