

Preparation of carbon nanotubes by use of polymer blend method

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Abstract

We are trying to prepare carbon nanotubes (CNT) by using polymer blend technique. After a copolymer of PAN-co-PMA was confirmed to be spun, the core-shell particles consisting of PMMA as a core and PAN-co-PMA as a shell were prepared and furthermore coated with PMMA shell. The ratio of PAN and PMA in the copolymer was changed, and also the spinning temperature was changed widely to prepare CNTs.

Keywords: Carbon nanofibers; Carbon nanotubes; Transmission electron microscopy, Microstructure

1. Introduction

Few years ago we proposed preparation of carbon nanotubes by use of core-shell polymer particles (Figure 1.) [1,2]. However, the core-shell particles phase-separated easily at melt-spinning process, leading to no formation of carbon nanotubes. In order to spin without the phase-separation, a centrifugal spinning machine was derived from a cotton candy machine, instead of a continuous melt-spinning apparatus. In particular, a mesh heater was developed to spin just immediately after melting of the core-shell particles. Also the rotor speed was increased from 500rpm to 5000rpm to increase the centrifugal force. The nanotubes were prepared by using of polymer blend method (Figure 2.).

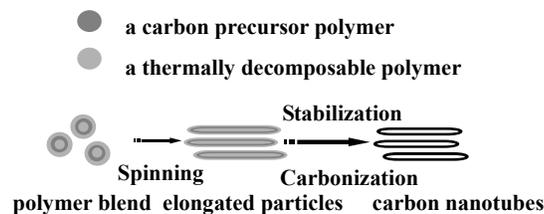


Figure 1. Preparation process of CNTs by spinning of coreshell polymer particles

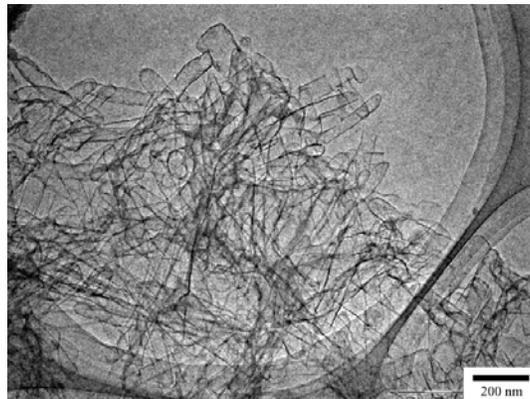


Figure 2. The previous prepared CNT by polymer blend technique.

We expected that the novel method was good for preparing nanotubes. But yield and reproducibility were not good. So we must considered the cause to improve that step by step. First we confirmed that a copolymer of polyacrylonitrile to be spun. Next we tried to prepare nanofibers by use of the core-shell particles consisting of PAN copolymer as a core and PMMA as a shell. Finally we tried to prepare carbon nanotubes.

Unfortunately, the centrifugal spinning machine was broken until now. So we couldn't advance the experiment. We would like to present more perfect results in the conference. We would like to present more honest results in the conference.

2. Experimental

As a carbon precursor polymer, a copolymer of polyacrylonitrile and poly (methacrylate) (PAN-PMA) with a mol ratio of PAN: PMA=95:5, 92.5:7.5, 90:10 were polymerized by the conventional soap-free polymerization method.

And then they were spun by the centrifugal spinning machine. The temperature and the rotation speed were 230~290°C and 5000rpm, respectively. The stabilization of the 5mol% copolymer was good, but spinning was not good. 7.5 and 10mol% copolymer was spun by the centrifugal spinning machine. So following the experiment, we use 7.5mol% copolymer.

Next the 7.5mol% copolymer particles were coated with a Poly (methyl methacrylate) (PMMA) in order to avoid the coagulation of PAN shell at the spinning process. The resulting core-shell particles were spun by the centrifugal spinning machine. The temperature and the rotation speed were 250°C and 5000rpm, respectively. The obtained fibers were stabilized at 220°C for 10h under an air atmosphere. Finally the stabilized fibers were carbonized at 1000°C for 1h in a nitrogen atmosphere. The samples were observed by a FE-SEM. The diameters of the obtained fiber were shown in Fig. 3. They had more than 1μm of diameters. But the original PAN copolymer particles were about 100nm in diameter, so phase-separation at the spinning process occurred.

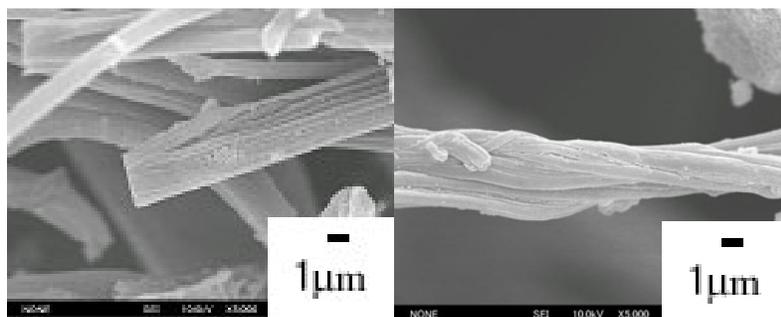


Figure 3. FE-SEM images of carbon products

Preventing phase-separation, 1.5 and 2 times PMMA were coated with PAN copolymer particles, and they were spun by the centrifugal spinning machine. The obtained fibers were stabilized and carbonized above condition. But the thicker PMMA, core PAN copolymer particles were not spun, only PMMA were spun. Because PMMA was easier spun than PAN copolymer. So we observed only carbon particles

We thought if the PAN copolymer particles include PMMA, such as PMMA/PAN copolymer core-shell particles, which are easier spun than PAN copolymer particles.

So the core-shell particles were coated with PMMA furthermore by polymerization. The resulting core-shell particles were spun by the centrifugal spinning machine at several temperature And the carbon products were observed by a FE-SEM and a TEM.

3. Results and discussion

Fig.4 shows carbon products (spinning temperature 250 °C) by the FE-SEM. The diameters of fibers were 200 nm and lengths were about 3μm.

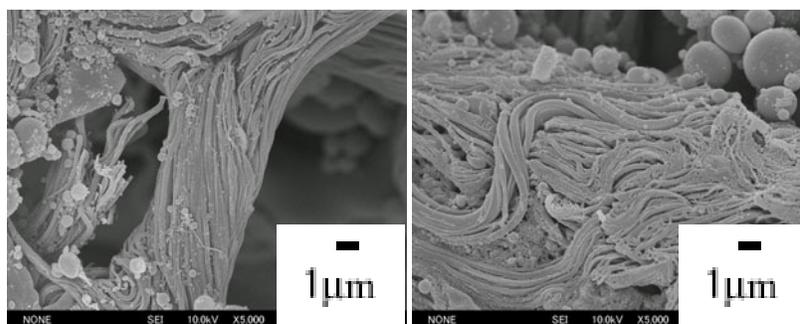


Figure 4. FE-SEM images of carbon products

Fig.5 shows carbon products by the TEM. There was no hollow in carbon products. Because the phase-separation was occurred. at spinning process.

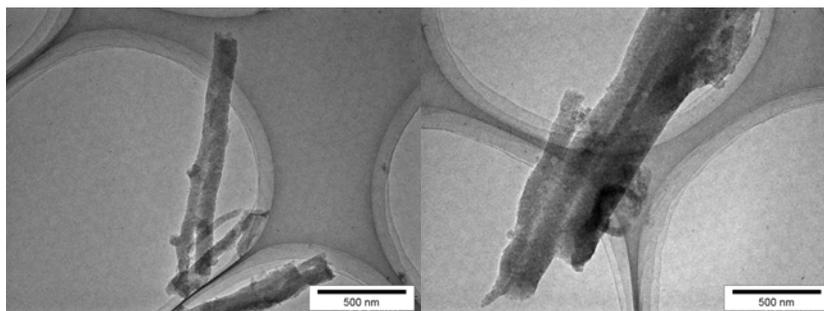


Figure 5. TEM images of carbon products

We are really sorry it was difficult to coat a copolymer of PAN-PMA as a shell neatly. So it was hard to get nanoballoons after carbonization. Reproducibility was not good. We thought the reason why the affinity of PMMA core and PAN-co-PMA polymer of polyacrylonitrile and poly (methyl methacrylate) as a shell now. Because we thought it has higher affinity than PAN-PMA. And we should try again that by using of the core-shell particles that had thinner than previous PAN copolymer shell. Nevertheless changing new copolymer, it was difficult to be coated thinner it, such as only thicker shell shown as Fig. 6.

And we should examine a polymer composition because each of core-shell particles are different viscosity at spinning process. But we don't know the combination of similar viscosity of a polymer that could polymerize as a shell. So we should try to use polymer that has high spinning temperature as a shell. We will coat polycarbosilane type U (m.p.300°C) for shell by solvent. If it is spun by the centrifugal spinning machine at low temperature, the core-shell particles is spun by the outermost polycarbosilane shell.

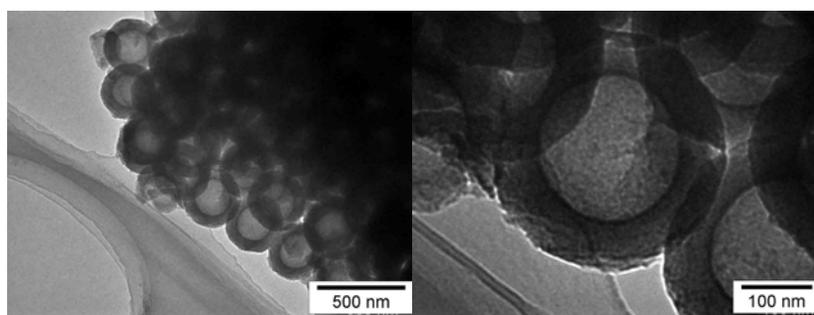


Figure 6. TEM images of carbon nanoballoons

4. Conclusions

It is still difficult that CNT is made by the centrifugal spinning. That has many problems. For example, it should be used the core-shell particles of similar viscosity. And it is also important to use the heat-resistant core-shell particles. Unless we couldn't solve the problems, this method has no future.

References

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