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Change in Morphology of Polyhydroxyamide, Polybenzoxazole and Carbon Particles by Thermal Treatments

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Abstract: Polyhydroxyamide particles consisting of 4,4'-diamino-3,3'-dihydroxybiphenyl and *m*-phthalyl chloride were prepared by a precipitation polymerization method. The particles were porous spherical particles with an average diameter of ca. 1 µm. And the polyhydroxyamide particles were transformed into polybenzoxazole particles through the ring-closing reactions by the thermal treatment at 360 °C for 3 h. The polybenzoxazole particles were the rugged spherical particles, but remained unchanged in the size. The thermal decoposition temperature at 5wt% loss was estiamted to be 607 °C. Also, the degrees of crystallinity for the polyhydroxyamide and polybenzoxazole particles were high. Further, the polybenzoxazole particles were transformed into carbon particles by the thermal treatment up to 1000 °C. The morphology changed from rugged surface to smooth surface. However, the diameter was almost kept. Thus, the submicron-sized polyhydroxyamide, polybenzoxazole and carbon particles obtained were found to change the morphology and property by thermal treatments.

Keywords: Carbon particle, morphology, polybenzoxazole, polyhydroxyamide, property, submicron-size, thermal treatments.

1. INTRODUCTION

Submicron-sized polymer particles have received much attention for practical applications such as medical carriers, chromatographic carriers, material modifiers and coating agents [1-5]. The morphology of the particles have significant influences on the separation ability and insulation characteristics and so on the products as it is closely correlated with the surface area and the porosity. Also, unique and excellent characterisitic features and functions are required to satisfy novel applications. Thus, it is important and useful to create submicron-sized novel polymer particles and control the morphology and characterisitic features.

Polyhydroxyamide (PHA) is aromatic polyamide with hydroxyl groups and a precursor of polybenzoxazole (PBO). It has excellent mechanical property and solvent resistance [6-10]. Also, the hydroxyl groups have a high affinity for water and induce an interaction between molecular chains. Thus, it is thought that PHA can be used for high functional particles by designing the structure. On the other hand, PBO has excellent thermal and mechanical properties and solvent and flame resistances, which are mainly used in fiber form [10-13]. In particular, PBO fibers show the highest tensile strength and modulus among all the commercial polymer fibers. Thus, they have been applied for flack jacket and reinforcement material. However, it is difficult to fabricate PHA and PBO particles in a secondary process because of excellent mechanical property and solvent resistance. Thus, submicron-sized PHA and PBO particles have not been previously reported. Therefore, the particles are expected to create novel and specific applications. Meanwhile, carbon materials have excellent electrical property and thermal conductivity. Thus, submicron-sized carbon particles are also expected to be used for specific and high performance applications. However, it is not so easy to obtain submicron-sized carbon spherical particles, because in many cases the spherical particles are transformed into the formless materials by the thermal treatment.

We have previously established the precipitation polymerization method using ultrasonic irradiation to prepare some types of nano- and submicron-sized aromatic polyamide particles [14,15]. Recently, submicron-sized aromatic polyamide with functional groups, polyhydroxyamide (PHA), particles were obtained. And they were transformed into PBO and carbon particles by thermal treatments. The three types of particles were almost the same in the size, but were different in the morphology. Thus, in this paper the morphologies and characteristic features of the PHA, PBO and carbon particles obtained by thermal treatments were reported.

2. MATERIALS AND METHODS

4,4'-Diamino-3,3'-dihydroxybiphenyl and *m*-phthalyl chloride were purchased from Tokyo Kasei Co., Japan. The reaction solvent acetone was purchased from Kishida Chemical Co., Ltd., Japan. These compounds and solvent were used as received without any further purification.

2.1. Preparation of Polyhydroxyamide Particles

4,4'-Diamino-3,3'-dihydroxybiphenyl (0.0005 mol) and *m*-phthalyl chloride (0.0005 mol) were dissolved in 50 ml

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acetone, respectively. 5ml distilled water was added to the 50 ml 4,4'-diamino-3,3'-dihydroxybiphenyl solution, and then the entire *m*-phthalyl chloride solution was added at once. The solution was subjected to ultrasonic irradiation at 28 KHz in a water bath while mixing for a period of 30 min. The product was extracted by centrifugal separation and washed five times with acetone and water to remove any unreacted monomer. The sample was dried in a vacuum oven at 100 °C for 2 h and room temperature for 12 h.

2.2. Preparation of Polybenzoxazole and Carbon Particles

For polybenzoxazole particles, polyhydroxyamide particles were kept at 100 °C for 1 h and then heated up to 360 °C at a rate of 10 °C / min, followed by keeping for 3 h. Meanwhile, for carbon particles, polybenzoxazole particles were kept at 100 °C for 1 h and then heated up to 1000 °C at a rate of 10 °C / min. These thermal treatments were performed under a nitrogen atmosphere using the TG/DTA analyzer.

2.3. Characterization

Infrared spectra were measured using a PerkinElmer Spectrum One infrared spectrometer (PerkinElmer Ltd., USA) in KBr tablets at a resolution of 4 cm^{-1}. Thermal treatments and TG/DTA measurements were carried in a nitrogen atmosphere using a SII Nano Technology TG/DTA 6300 analyzer (SII Nano Technology Inc., Japan). The particles obtained were sputtered with a gold coating, and their morphologies were investigated using a Hitachi Fe-SEM S-4700 scanning electron microscope (SEM) (Hitachi Ltd., Japan). X-ray diffraction profiles were obtained using a Rigaku RINT-2500 X-ray diffractometer (Rigaku Ltd., Japan) with graphite monochromatized Cu-Kα radiation and a scan speed of 1 °/min.

3. RESULTS AND DISCUSSION

3.1. Thermal Treatment and Chemical Structure

The curve a in Fig. (**1**) shows the infrared spectrum of the sample in the region of 450 – 4000 cm^{-1}. For the sample, characteristic bands attributed to polyamide were observed: for example, 3215 cm^{-1} [amide A (N-H stretching mode)], 1650 cm^{-1} [amide I (C=O stretching mode)], and 1517 cm^{-1} [amide II (coupling of C-N stretching and N-H in-plane bending modes)][16]. In addition, bands were detected at 3400 cm^{-1} and 1408 cm^{-1}, corresponding to the O-H stretching mode and the C-O-H bending mode of hydroxyl groups (-OH), respectively [17]. Thus, the sample obtained was determined to consist of aromatic polyamide with hydroxyl groups, polyhydroxyamide (PHA). The reaction for the precipitation polymerization is shown in Scheme (**1a**) and the sample obtained is noted as PHA.

Fig. (**2a**) shows the thermogravimetric (TG) and differential thermal analyses (DTA) curves of the PHA sample in the temperature region of 100 - 1000 °C. The PHA sample was kept at 100 °C for 1 h prior to a measurement and then measured at a rate of 10 °C / min under a nitrogen atmosphere. The TG curve decreased gradually in the temperature region of 140 - 360 °C and further changed significantly at ca. 600 °C. Meanwhile, The DTA curve showed a strong endothermic peak at 315 °C and a weak endothermic peak at 590 °C. It is thought that the decrease of the TG in the temperature region of 140 - 360 °C is derived from the evaporation of H_2O generated in the ring-closing reactions as shown in Scheme (**1b**) [18]. Also, the ratio of weight loss estimated by the TG curve, 11%, was in good agreement with the theoretical value. Based on the result, the PHA sample was heated at 360 °C for 3 h under a nitrogen atmosphere to complete the ring-closing reactions. Fig. (**2b**) shows the TG and DTA curves of the sample obtained after the thermal treatment. They showed the changes similar to those of the PHA sample at ca. 600 °C. The temperature is thought to be correlated with the thermal decomposition [6,7]. Thus, the thermal decomposition temperatures at 5 wt% loss and at 10 wt% loss were estimated to be 607 °C and 632 °C, respectively, indicating excellent thermal resistance [12,19]. Meanwhile, the change in the temperature region of 140 - 360 °C was not detected for the TG and DTA curves. It has been previously reported that the endothermic enthalpies of the peak at 315 °C decreased as the number ratios of the ring-closing increased [6]. Also, the flat plateau in TG curve indicates that the H_2O was not generated. Thus,

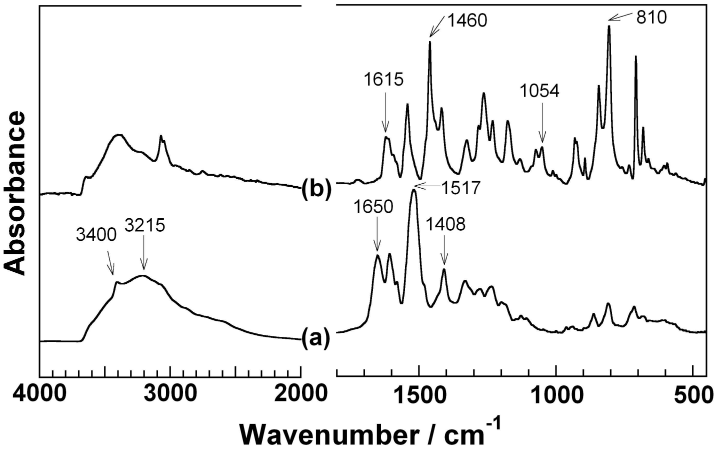
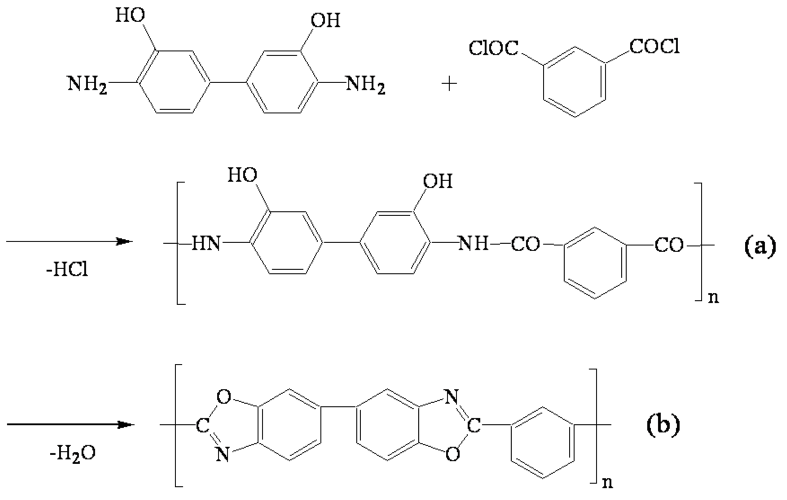


Fig. (1). Infrared spectra in the region 450-4000 $cm^{-1}$of: (**a**) PHA and (**b**) PBO particles.



Scheme 1. Reactions; (**a**) from monomers to polyhydroxyamide and (**b**) from polyhydroxyamide to polybenzoxazole.

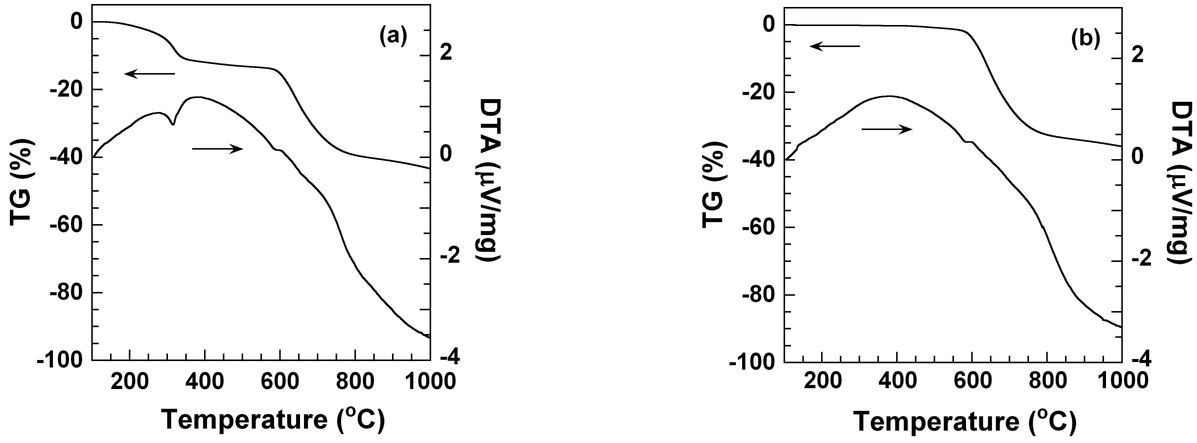


Fig. (2). Thermal diagrams of: (**a**) PHA and (**b**) PBO particles.

it is concluded that the ring-closing reactions did not occur because they completed perfectly by the previous thermal treatment.

The curve b in Fig. (**1**) shows the infrared spectrum of the sample obtained after the thermal treatment at 360 °C for 3 h. Characteristic bands attributed to benzoxazole rings appeared at 1615 cm^{-1}, 1460 $cm^{-1}$and 1054, 810 cm^{-1} [12,13, 20, 21]. On the other hand, the amide I band at 1650 cm^{-1} detected for the PHA sample disappeared. Based on the TG/DTA and IR results, it is thought that the PHA sample changed to polybenzoxazole completely through the ring-closing reactions (Scheme **1b**). The product obtained after the TG/DTA measurement up to 1000 °C was confirmed to be carbon by the infrared spectrum (not shown).

In the following section, the sample obtained by heating the PHA sample at 360 °C for 3 h is noted as PBO and the product obtained after the TG/DTA measurement up to 1000 °C (Fig. **2b**) is noted as carbon.

3.2. Morphology

Fig. (**3 a-f**) show SEM images of the PHA, PBO, carbon samples, respectively. All the samples were spherical particles with average diameters of ca. 1 µm. The diameters were almost kept and the new connection between the particles generated by thermal treatments was not observed. On the other hand, the surface morphology changed significantly. That is, the porous PHA particles (Fig. **3 a** and **d**) were transformed into the smooth carbon particles (Fig. **3 c** and **f**) *via* the rugged PBO particles (Fig. **3 b** and **e**). It is speculated that the pore on the surface decreased gradually in the size and then disappeared during the thermal treatments. Although the details about the morphology inside the particle and the formation mechanism have not been clarified yet, they will be revealed in the near future. Thus, the surface morphology was found to change by thermal treatments.

3.3. Degree of Crystallinity

Fig. (**4 a-c**) show X-ray diffraction patterns of the PHA, PBO and carbon particles. In the pattern for the PHA particles two sharp peaks at $2\theta=15°$ and 25° were observed [6]. On the other hand, in the pattern for the PBO particles, some new peaks appeared except the two sharp peaks detected at the same positions for the PHA particles. It has been previously reported that the peak at $2\theta=15°$ is corresponding to (200) reflection and the splitting peaks at $2\theta=25$ and 26° are corresponding to (110) and $(1\bar{1}0)$

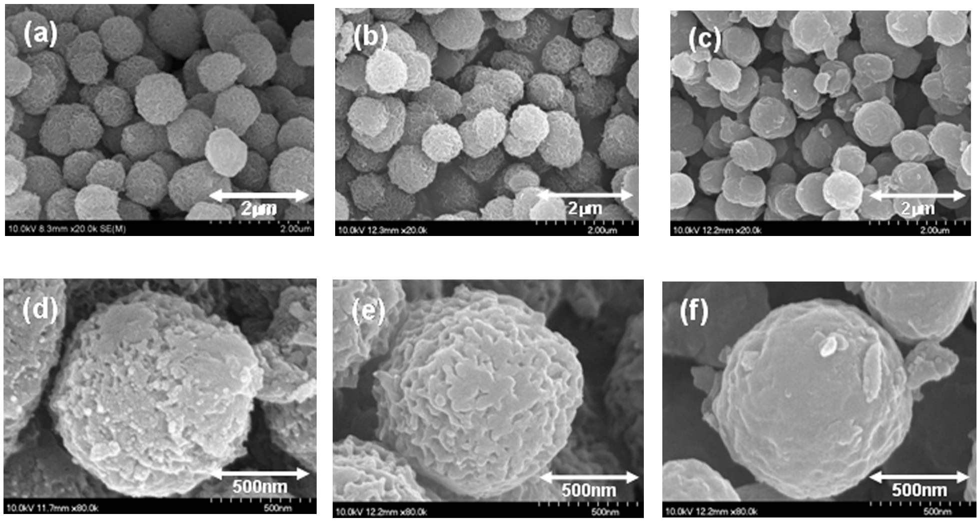


Fig. (3). SEM images of: (**a**) PHA, (**b**) PBO and (**c**) carbon particles and enlarged SEM images of: (**d**) PHA, (**e**) PBO and (**f**) carbon particles.

reflections [11]. Thus, it is speculated that the splitting peaks are originated from the change in the crystal structure result by the transformation from PHA to PBO. However, all the new peaks detected can not be assigned at the present stage. An additional X-ray structure analysis will be required for the detail assignment. Based on these sharp peaks, the PHA and PBO particles were found to show high degrees of crystallinity [22].

Meanwhile, in the pattern for the carbon particles one broad peak was observed. Thus, the carbon particles were found to be amorphous [19].

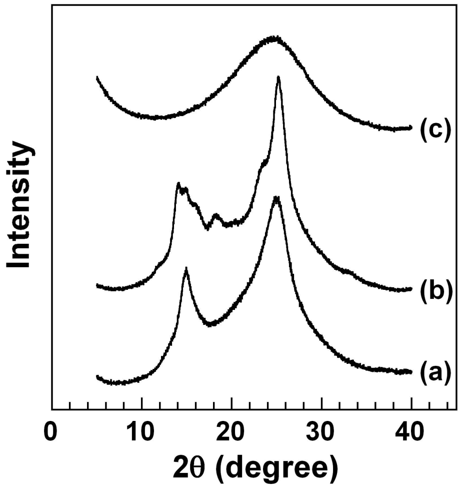


Fig. (4). X-ray diffraction patterns of: (**a**) PHA, (**b**) PBO and (**c**) carbon particles.

CONCLUSION

Polyhydroxyamide (PHA) particles have been prepared from 4,4'-diamino-3,3'-dihydroxybiphenyl and *m*-phthalyl chloride by the precipitation polymerization method. The particles were porous spherical particles with an average diameter of ca. 1 μm. And the PHA particles were transformed into polybenzoxazole (PBO) particles through the ring-closing reactions by the thermal treatment at 360 °C for 3 h. The PBO particles were the rugged spherical particles, which diameter was almost kept. The thermal decoposition temperature of the PBO particles was estiamted to be 607 °C at 5 wt% loss, indicating excellent thermal resistance. The degrees of crystallinity for the PHA and PBO particles were high. Further, the rugged PBO particles were transformed into the smooth carbon particles by the thermal treatment up to 1000 °C, which size was almost kept. Thus, the submicron-sized PHA, PBO and carbon particles obtained were found to change the morphology and property by thermal treatments. The change in the morphology is effective for controlling the surface area and the porosity of the particles. The transformation from the porous particles into the non-porous particles is expected to be available for the preparation of the particles composited with other materials.

CONFLICT OF INTEREST

Declared none.

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