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LETTER

Glass-like carbon derived from a polymer consisting of furfuryl alcohol and tetraethylene glycol

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Introduction

Glass-like carbons are generally made from precursors such as furan and phenol resins through carbonization and heat treatment. These carbons are used in many fields as parts for semiconductor production, separators for fuel cells, and multipurpose crucibles due to their superior strength, non-dissipation, non-permeability, and excellent oxidation resistance [1]. However, glass-like carbons have unavoidable issues in terms of cost performance and difficulty in making thick bodies. The difficulty is due to a problem encountered in the escape of the decomposed gases. The excessive cost arises from the long time required for carbonization. Since precursors such as furan and phenol resins generate a large quantity of the decomposed gases and considerably shrink during carbonization, cracks, and ruptures are brought in the specimens carbonized with high heating rates. Therefore, very low heating rates for carbonization are necessary. Furthermore, water produced during polymerization is known to induce the formation of macro pores [2], which impedes the production of glass-like carbons with high strength and high density. Applications for molding using a centrifuge, ultrasonication, and HIP have been attempted to create dense thick carbons [2, 3]. However, these methods cannot adopt higher heating rates for carbonization to create thick carbon material.

Polymer blend method for producing porous carbons has recently been investigated [4]. The system using furfuryl alcohol (FA) and tetraethylene glycol (TEG) is known to generate carbon with homogeneous micropores. Moreover, it is noteworthy in that the pore structure is interconnected [5]. This system expected to be very dense carbon when heated at high temperatures since micropores are reported to decrease with an increase in the heat treatment temperature. The pores in carbons made from an FA-TEG blend are anticipated to be helpful the gases generated during carbonization to escape. This would suggest that thick carbon bodies without cracks can be manufactured even with high heating rates for carbonization. In this article, the possibility of producing thick carbon material is investigated.

Experimental

Polymer as a precursor was prepared as follows. *p*-toluene (2 mass%) was added as a curing agent to TEG and stirred for 24 h at room temperature. Furfuryl alcohol of 100 mass% was then added and stirred at 0 °C for 1 h. Curing was performed under ultrasonic wave irradiation of 400 W at 50 °C for 24 h. To compare with the general production method, an FA-only polymer was also prepared at 50 °C for 72 h. The polymer obtained from the FA-TEG blend was carbonized at 400, 500, 700, and 1,000 °C for 2 h. Heating rates of 7 and 21 °C/h up to the prescribed temperature were selected. In addition, firing at 1,500 and 2,000 °C was conducted using a specimen fired at 1,000 °C. A heating rate of 200 °C/h was used in this preparation since an extremely slow heating rate for firing above 1,000 °C was not considered to be required. The heating processes were conducted in an argon stream of

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50 cc/min. The carbon specimens obtained at heating rates of 7 and 21 °C/h are hereafter referred to as FA-TEG7 and FA-TEG21. A heating rate of 2 °C/h for carbonization below 1,000 °C was used to prepare carbon via FA-resin without TEG, since the carbons obtained at rates of 7 and 21 °C/h shattered. This carbon is referred to as FA2. The initial amounts of raw materials were adjusted so that the final products would be 5 mm thick after heat treatment at 2,000 °C.

Results and discussion

Figure 1 depicts the changes in the surface areas of FA-TEG7 and FA2 heat-treated at between 400 and 2,000 °C. The data of the results of FA-TEG21 is omitted here because they were almost the same as those of FA-TEG7. The surface areas of both specimens reached a maximum at 700 °C and decreased steeply above 700 °C. The FA-TEG7 specimens were larger than those of the FA2 specimens over the entire temperature range. In particular, the surface areas of the FA-TEG7 specimens were about three times those of FA2 in temperatures ranging from 400 to 700 °C. It is known that carbons obtained from polymer blend composed of two polymers that one polymer yields carbon through thermal decomposition and the other polymer disappears by heat-treating have relatively high surface areas [5]. The reason for the high surface areas has been thought that the latter polymer leaves vacancies to be pores by disappearing. In this study, the high surface area is considered to be due to TEG to be volatilized. The gas permeability of the FA-TEG specimen heat-treated at 2,000 °C was measured to be 1.60×10^{-10} cm^2 S^{-1}. Compared to the typical glass-like carbons of which the values are reported to be in the range 10^{-7}–10^{-12} cm^2 S^{-1} [1], that value was evaluated to be in almost the same level. In Fig. 1, the surface area of FA-TEG7 heat-treated at 2,000 °C is somewhat larger than that of FA, indicating that the micropores are interconnected to some extent but they are closed. The detailed measurement and discussion regarding the gas permeability will be reported in future.

Figure 2 depicts the changes in volume contraction rate of FA-TEG7 and FA2 heat-treated at temperatures between 400 and 2,000 °C. The volume contraction rates of FA-TEG7 are almost equal to those of FA2 below 700 °C, but those of FA-TEG7 are significantly lager than FA2 above 1,000 °C. The volume contraction rate at 2,000 °C was 72% in FA-TEG7 whereas FA2 was 48%. Figure 1 also means that the porosity of FA-TEG7 is larger than that of FA2. The larger constriction rate seen in FA-TEG7 at high temperatures is considered to be dependent on the higher porosity.

SEM photographs of polished-carbon specimens heat-treated at 2,000 °C are presented in Fig. 3(a) FA-TEG7, (b) FA-TEG21, and (c) FA2. The large voids with size of about 10 μm are observed in FA2, whereas no hole is observed in FA-TEG7 and 21 specimens. The voids in FA2 are thought to be based on the sites formed during polymerization, since polymerization of FA produces cohesive the water through a dehydration-condensation reaction. The carbon obtained from the FA-TEG system was considered to have no pores with such size since water formed during polymerization of FA-TEG does not cohere due to TEG being hydrophilic.

The results of the 3-point bending-strength test are illustrated in Fig. 4. The averages of bending strength in FA-TEG7, FA-TEG21, and FA2 were 130, 115, and 100 MPa. The average bending strength of FA2 was

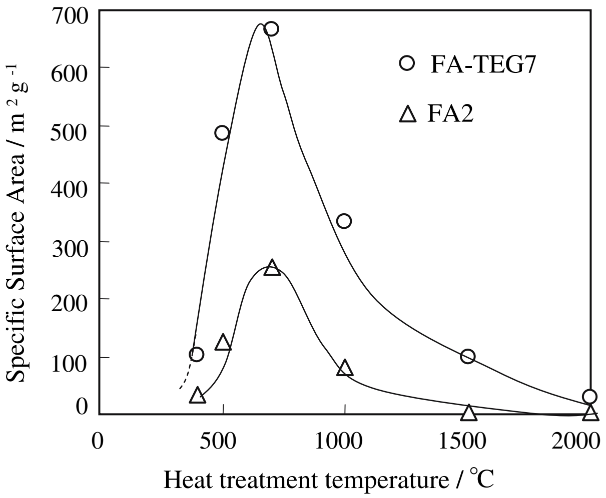


Fig 1 Specific surface area of specimens as a function of heat treatment temperature

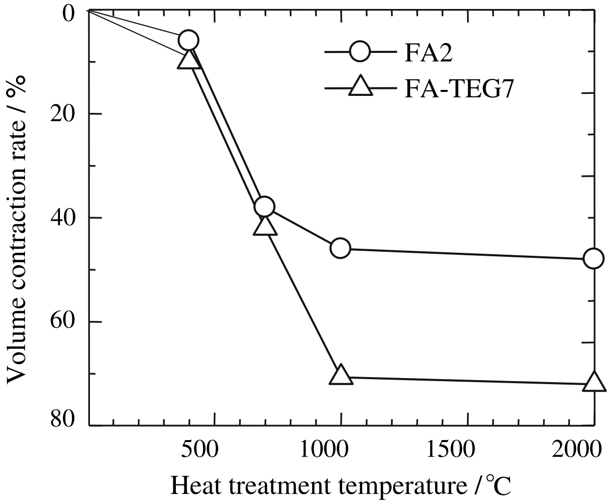
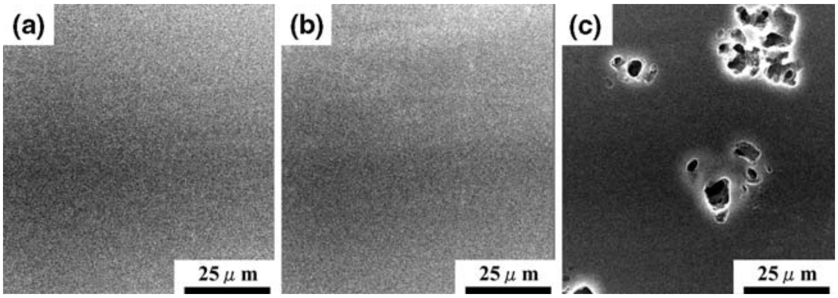


Fig 2 Volume contraction rates of specimens as a function of heat treatment temperature

Fig 3 SEM photographs of bulk specimens heat-treated at 2,000 °C: (**a**) FA-TEG7, (**b**) FA-TEG21, and (**c**) FA2



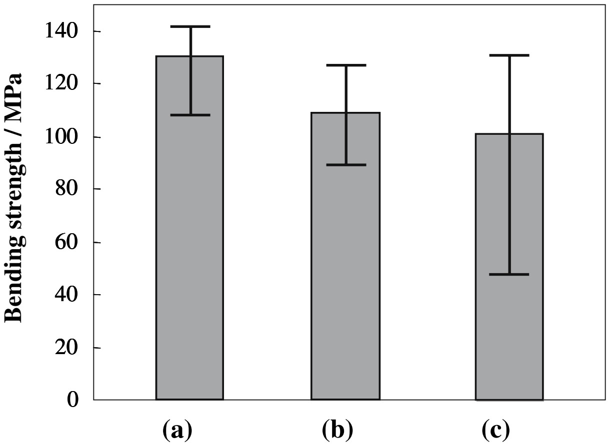


Fig 4 Bending-strength of bulk specimens heat-treated at 2,000 °C: (**a**) FA-TEG7, (b) FA-TEG21, and (**c**) FA2

somewhat lower than those of the FA-TEG system and the scattering range was wide, which is because that FA2 have many large voids as shown in Fig. 3c. The high strength of FA-TEG7 and FA-TEG21 is attributed to the dense texture without large voids as is observed in Fig. 3a and b. The value of the strength of typical glass-like carbon is reported to be in the range 100–130 MPa [1]. Comparing the data of FA-TEG7 and 21 with typical one proves that the strength of FA-TEG7 and 21 is sufficiently maintained even though the heating rate in the carbonization process was extremely high. This is considered to be attributable to the microstructures through which the decomposed gases can easily escape in the FA-TEG system.

In this study, we confirmed that thick bodies of glass-like carbon can be prepared when FA and TEG are used as raw materials of carbon precursors, even though the heating rate for carbonization is very high compared to ordinary processes.

References

1. Oya A (1996) Introduction to carbon materials, new edition. Carbon Society of Japan, Realize Inc., Tokyo, p 113
2. Cocchieri E, Scherbakoff N, Rezende M (2001) Carbon 39:45
3. Hoshi K, Tanabe Y, Yasuda E (1997) TANSO 184:199
4. Kyotani T (2000) Carbon 38:269
5. Wang Y, Tan SH, Jiang DL, Zhang XY (2003) Carbon 41:2065