

Carbon foams prepared from polyimide using urethane foam template

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Introduction

Polyurethane foams prepared in well-controlled pore structures have been used in huge amounts for seat cushion, heat insulation, shock absorbance, etc. [1]. However, their recycling system has not been established yet [2]. Through carbonization of these urethane foams, their characteristic morphology of foam was found to be lost and only flaky powders of carbon were obtained with a low carbon yield. On the other hand, it has been shown that polyimide films can result in carbon films through carbonization process without special cares [3]. The structure of resultant carbon films depends strongly on the molecular structure and their orientation of imide molecules, not only graphite films but also glass-like carbon films being able to be prepared [3,4]. Pore structure control in these polyimide-derived carbon films led to a high performance of molecular sieving carbon for the separation of hydrogen [5,6].

In the present work, therefore, urethane foams were selected as a template material and polyimide resin as carbon precursor in order to prepare the carbon foams. Water adsorption behavior was studied on the resultant carbon foams after activation in air and also supporting performance of photocatalyst anatase TiO₂ particles was examined.

Experimental

Into the poly(amide acid) solution prepared from pyromellitic dianhydride (PMDA) and 4,4-diamino-diphenyl ether (DDE) at room temperature, urethane foams were dipped for 1 h to impregnate. After impregnation, the foams were heated at 60 °C for 10 h in order to evaporate the solvent and then at 200 °C for 20 h in order to imidize the poly(amide acid). The urethane foams impregnated by polyimide were carbonized at 1000 °C for 1 h in a flow of high purity Ar gas. Pore structure in activated carbon foams was estimated by measuring nitrogen adsorption at -196 °C and BET surface area was calculated.

Water adsorption and desorption behavior of carbon foams thus prepared was studied by using TG apparatus, according to the same procedure reported in our previous paper [7].

Carbon foam with the size of about 10x10x2 mm³, which floated on the water, was mounted by anatase under hydrothermal condition. Anatase-loaded carbon foam thus prepared was added into 40 mL of aqueous solution of methyleneblue

(MB) with a concentration of 2.94×10^{-5} mol/L at room temperature. After kept the solution in the dark to saturate the adsorption, ultraviolet (UV) rays were irradiated from a lamp with 10 W power. The concentration change of MB in the solution was followed by measuring the absorbance at the wavelength of 650 nm of MB molecules.

Results and Discussion

Impregnation of polyimide into polyurethane foam

Polyurethane foams consisting of ether bonding were unable to be used as template for poly(amide acid) impregnation, because of the dissolution of the urethane foams themselves into the solvent DMAc. Into the ester-type urethane foams, on the other hand, poly(amide acid) was able to be impregnated and result in polyurethane/polyimide (PU/PI) composite foams after imidization at 200 °C.

After PI impregnation, the size of foams shrank about 20 %, but their appearance was kept porous. In Fig. 1a) and b), SEM images are compared on the starting urethane foam consisting of ester bonding and foam after impregnation of polyimide, respectively. Foam characteristics are kept after impregnation of PI component. In the case of template foam with very low bulk density of 0.06 g/cm^3 , amount of impregnated PI is not so large and the resulting PU/PI composite foam has also relatively low bulk density of 0.29 g/cm^3 . On the templates having higher bulk density as 0.16 g/cm^3 , larger amount of PI could be impregnated and the resulting PU/PI composite foams had higher bulk density of 0.35 g/cm^3 .

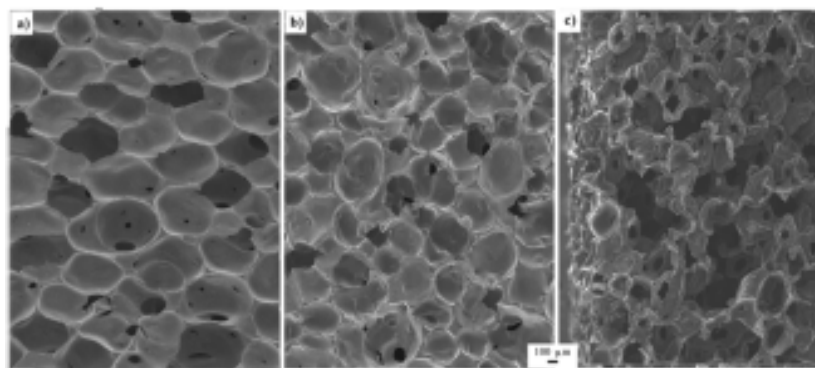


Fig. 1 SEM images. a) Original polyurethane foam, b) after impregnation of polyimide and c) after carbonization at 1000 °C.

Formation of carbon foams

PU/PI composite foams thus prepared were easily converted to carbon foams by heating above 800 °C. After carbonization at 1000 °C, the specimens shrank roughly 20 % along each side of tablet, but kept foam-like morphology, as shown in Fig. 1c). Bulk density of the carbon foams was in a range of $1.6 - 2.3 \text{ g/cm}^3$. Some of these carbon foams had apparently low bulk density and were hollow inside, which were found to float on the water

Graphitization of carbon foam

After 3000 °C treatment, the foam characteristics was kept, and its interlayer spacing d_{002} was 0.3367 nm and crystallite size $L_c(002)$ was 30 nm, revealing that

the foams prepared could be converted to graphite foams.

Possible applications

Water adsorption of carbon foam

Carbon foam activated at 400 °C for 1 h in air was subjected to the test of adsorption/desorption of water vapor by the following measurement of mass change in TG apparatus; heating up to 200 °C followed by cooling down to room temperature in a flow of dry N₂ gas and then changing to wet N₂ gas, which was bubbling in water kept at 40 °C. Mass change in this process is shown in Fig. 2.

Mass increase at room temperature is reasonably supposed to be due to adsorption of water vapor in wet N₂. In comparison with our previous result on carbon films [7], adsorption of water vapor occurs much more rapidly, mainly due to porous foam. Cyclability of water vapor adsorption is excellent.

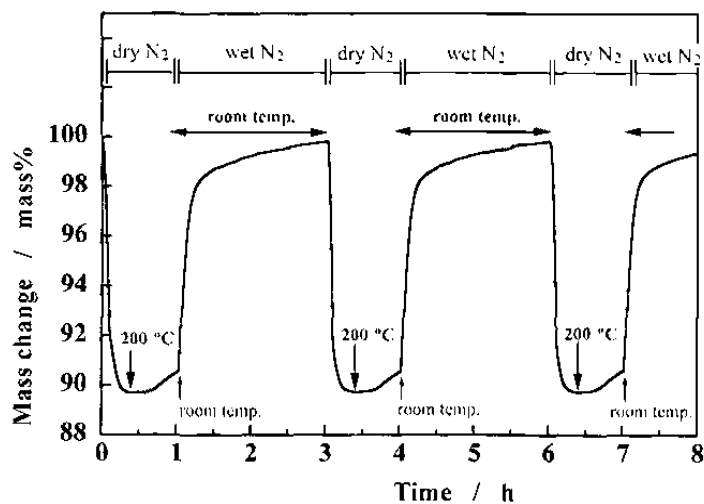


Fig. 2 Cyclic mass change due to desorption/adsorption of water vapor.

Loading of photocatalyst anatase onto carbon foam

Fine spherical aggregates, less than 100 nm, of minute anatase particles are covering the surface of carbon. Anatase loaded was about 3.2 mass%.

Change in concentration of methyleneblue in its aqueous solution with time is shown in Fig. 3. Even after anatase-loading, the carbon foam was floating on MB solution. The decrease in MB concentration in the dark is very low, revealing only small adsorption of MB. Under UV irradiation, however, concentration of MB decreases rapidly.

By selecting polyurethane template rich in closed pores, the resultant carbon foam can be hollow and so floating on the water. In the present work, this water-floating carbon foam was used for loading of photocatalyst anatase, from which high efficiency of photodecomposition of pollutants, methyleneblue in the present work, was expected, though it could not be demonstrated quantitatively. If the foam was used as substrate for anatase after activation, high adsorptivity of the pollutants could be expected in addition to photocatalytic activity, as anatase-loaded activated carbon showed [8].

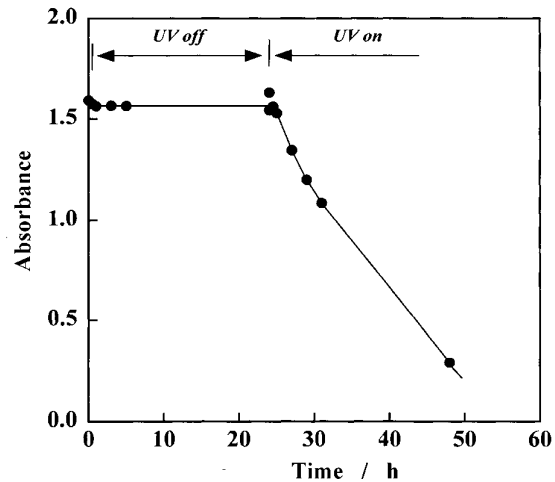


Fig. 3 Change in absorbance at 650 nm wavelength of methyleneblue in the coexistence of anatase-loaded carbon foam with and without UV irradiation

Conclusion

Carbon foams were successfully prepared using polyurethane foams as a template. Polyurethane/polyimide (PU/PI) composite foams prepared by impregnating poly(amide acid) could convert to carbon foams by heating above 800 °C. Graphite foams with relatively high graphitizability were prepared by heat treatment at 3000 °C. Two applications of these carbon foams, *i.e.*, an adsorbent of ambient water vapor and a substrate for photocatalyst anatase TiO₂, were proposed through preliminary experiments.

Acknowledgement

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