

POROUS CARBON PREPARED FROM POLYMER BLEND FILMS

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INTRODUCTION

Porous carbon materials are used in a wide range of applications, including adsorbents and catalyst supports. Electrochemical applications of these materials in electrolytic processes such as battery and fuel cells require porous surface structures that allow good contact with the chemical species involved [1,2]. Macroporous carbons have been prepared from polyimide by a phase inversion method [3]. Since this polymer is highly heat-resistant and can easily be transformed into a carbonaceous material, maintaining the shape and pore structures of the polymer, the pore size distribution of the carbon products can be designed by controlling at the polymer stage.

In this study we attempted to prepare porous carbon films with homogeneous pores from the polyimide blended with an aliphatic polymer which leaves voids by the decomposition.

EXPERIMENTAL

Two types of polyimides and aliphatic polymers were used by taking their compatibility into account; one polyimide is poly(4,4'-oxydiphenylene pyromellitimide) (PI) and the other poly(diphenylene pyromellitimide) (PP). N,N-dimethylacetamide (DMAc) solution of polyamic acid corresponding to each polyimide was blended with that of poly(methyl methacrylate) (PMMA) or poly(ethylene glycol) (PEG). The structure of these polymers is shown in Fig. 1.

The polymer film prepared according to the method described previously [4] was imidized at 200°C in vacuo and then carbonized at 600°C for 1 h at a heating rate of 3°C/min in an argon stream.

RESULTS AND DISCUSSION

The combination of PI and PMMA gave an opaque film when blended in equal ratio. The blend film was washed with DMAc in order to remove PMMA

from the film by extraction. From the observation of the treated film by scanning electron microscope PMMA was found to be present in the form of disperse phase due to the phase separation. The similar morphology was also seen when PI-PMMA film was heat-treated at 600°C. The thermogravimetric analyses of PI and PI-PMMA films reveal that PI and PMMA are independently pyrolyzed in the blend film. This means that no interaction between PI and PMMA takes place during the heat-treatment. Nitrogen adsorption isotherm experiments were carried out for PI and PI-PMMA films treated at 600°C. The results indicate that both curves are very similar and of Langmuir type.

When PEG was used as a substitute for PMMA, the film prepared became transparent, suggesting homogeneous blending. However, heat-treatment up to 600°C did not bring about additional formation of micro- or mesopores. It is presumed in this case that thermal motion of PI molecules at high temperature causes blocking of the small voids which are formed by the decomposition of PEG. Thus, PI was replaced by PP because the glass transition temperature of PP is too high to be determined due to its rigid structure. This blend polymer (PP-PEG) also gave a transparent film. Nitrogen adsorption and desorption isotherms of the carbonized film were shown in Fig. 2(a), along with those of PP alone. The carbon film from the blend polymer shows different adsorption and desorption behaviors from that of PP carbon. Another feature of this film is to exhibit a hysteresis curve. The pore size distribution was obtained from these curves by Cranston-Inkley method (Fig. 2(b)). The curve from PP-PEG carbon gives a peak at ca. 4.3 nm, suggesting the existence of opening pores with this size. On the other hand, it was found from the examination of this sample by transmission electron microscope that many small pores with diameter of ca. 10 nm are

homogeneously dispersed in spherical shape, as can be seen in Fig.3.

In conclusion the carbon film from PP-PEG blend polymer gave a unique pore structure in which spherical pores of 10 nm are connected to each other at opening pores of 4.3 nm.

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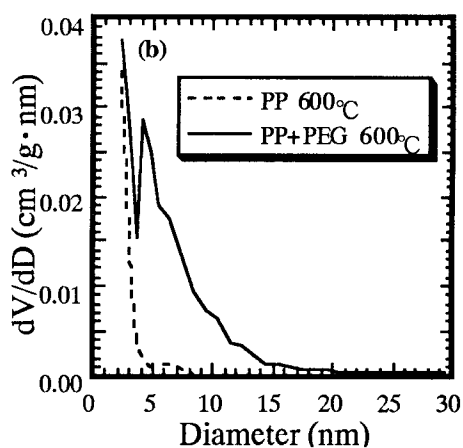
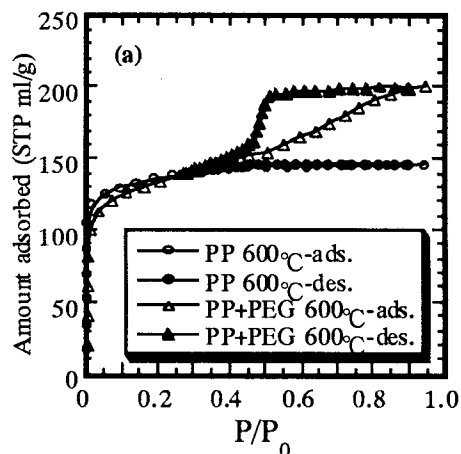


Fig. 2 (a) N_2 isotherms (77K) and (b) pore size distribution of PP and PP-PEG films heat-treated at 600°C

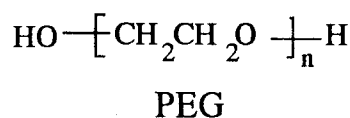
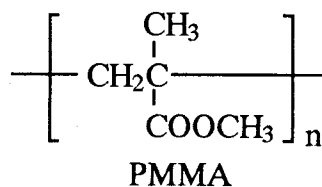
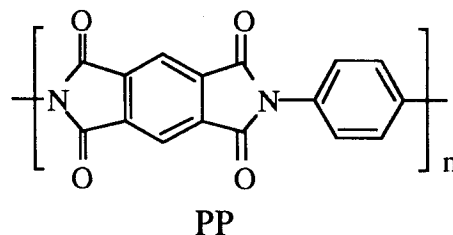
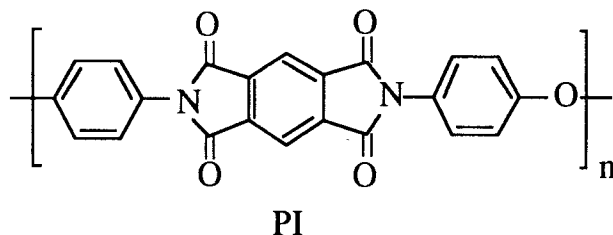


Fig. 1 The structure of polyimides and aliphatic polymers

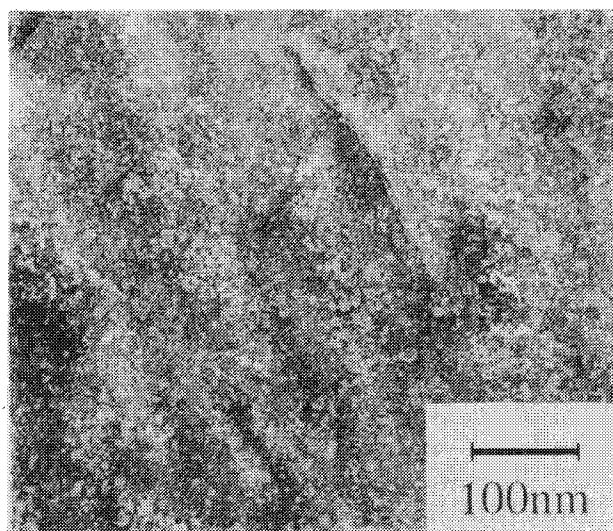


Fig. 3 TEM micrograph of PP-PEG films heat-treated at 600°C