Preparation and characterization of carbon materials from phenol formaldehyde resin with pore forming substance

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Abstract

This paper describes the carbonization behavior of phenol-formaldehyde resin (PF) blended in the presence of simple organic substances of m-phthalic acid (PA), trimesic acid (TMA) and phloroglucinol (PG). The weight loss and heat flow were monitored in order to study their carbonization behavior by thermogravimetric analysis (TG) and differential scanning calorimetry (DSC), respectively. These organic additives showed some interactions with PF during heat treatment up to 1273 K in a flowing argon. The temperature range, at which interactions occurred, depended upon the type of pore formers. Examination of TGA and DSC results indicates that effectiveness of interaction between pore former and PF at their interface is as follows: PG>TMA>PA. It is suggested that phenolic group in pore formers interacted strongly with PF than carboxylic group does, thus changing the carbonization behavior during heating process of PF resin.

1.Introduction

Blending method has been studied as a possible method to prepare porous carbon materials without further activation. This method includes a manner, which pore former is blended in carbon precursor. The pore former decomposes during heat treatment, leaving pores in carbon matrix. Hatori et al. [1, 2] and Takeichi et al. [3, 4] applied blending method to prepare carbon films, which possess mesopores and macropores. They used polyimide membranes as a carbon precursor. Oya et al. [5,6] prepared mesoporous carbon fiber from phenol formaldehyde resin as carbon precursor, suggesting that the blending method leads to the possibility of modifying pore surface. Horie et al. [7, 8] loaded metals onto pore surface by carbonizing phenol-formaldehyde resin that was blended with pore former containing Pt(Ⅱ)-acetylacetonate. On the other hand, Horikawa et al. [9] reported that there was an interaction between phenol formaldehyde resin and pore former, resulting in the decomposition of pore former and the formation of pores. In our preliminary experiments, we found carbon precursor derived from phenol formaldehyde resin blended with benzoic acid yielded higher carbon residue than the expected yield calculated from the ratio of PF and benzoic acid [10]. It was because their carbonization behavior was affected by interactions between phenol formaldehyde resin and benzoic acid. Our final goal is to control pore surface structure by using these interactions at interface between carbon precursors and pore formers. Therefore, it is important to investigate their carbonization behavior. In this paper, we use phenol formaldehyde resin (PF) as a carbon precursor and simple organic
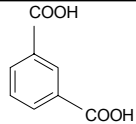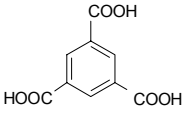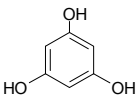
substances as a pore former, and studies interactions between PF and organic substance by using thermogravimetric analysis (TG) and differential scanning calorimetry (DSC).

2.Experimental

2-1. Materials

Phenol formaldehyde resin (Gun-ei chemical Ind. Co: PF) was used as the carbon precursor. Pore formers, which have several functional groups of phenolic and carboxylic groups. The pore formers used in this study were as follows; m-phthalic acid (Wako chemical Co. Ltd., designated as PA), trimesic acid (Wako chemical Co. Ltd., TMA) and phloroglucinol (Wako chemical Co. Ltd., PG). **Table 1** is a summery of pore formers studied in the present work.

Table 1 Summery of pore former studied in this work

Substance	Abbreviation	Molecular structure	Empirical formula	Melting point* [K]
m-phthalic acid	PA		$C_8H_6O_4$	623
trimesic acid	TMA		$C_9H_6O_6$	653
phloroglucinol	PG		$C_6H_6O_3$	489 – 492

* literature values

2-2. Sample preparations

PF was mixed separately with three types of pore formers in methanol at a weight ratio of PF to pore former as 2:1. These polymer blends were subjected to evaporation under vacuum to remove methanol remaining in the blends. Resulting mixtures were heat treated in air at 353 K in order to thermoset the blends for one day. The mixtures were then crushed mechanically into particles ranging from 425 μ m to 665 μ m, and they were further heat treated at 353 K to insure the complete removal of methanol. The samples thus prepared were identified by listing the type

of pore former, e.g., a sample prepared with a pore former of TMA in PF is reported as TMA/PF.

2-3. Analysis

Carbonization behavior on each of PA/PF, TMA/PF, PG/PF mixed polymer and corresponding pore formers was studied by thermogravimetric analyzer (TG) and differential scanning calorimetry (DSC), both of which were operated at a constant heating rate of 5 K/min in flowing argon.   Before subjected to their measurements, the samples were dried at 343 K for 4hrs in argon atmosphere and pore formers were dried at 303 K for 1h in argon atmosphere.

Temperatures in TGA and DSC were calibrated with standard sample. The calibration of TGA was based on measuring the curie temperature of nickel, and that of DSC was performed by measuring the onset temperature of fusion and the heat of fusion on indium and zinc metal. However, direct comparison of TGA and DSC data based on temperature may be incorrect in our case since the way of heat supplies is different between TGA and DSA apparatus.

3. Results and discussion

Fig.1 shows the TG curves of the PF and three pore formers (PA, TMA and PG). The PF showed a gradual weight decreased at 573-673 K and resulted in 58 wt% carbon residue after heating to 1273 K. The PA indicated a drastic decrease at around 600 K, and eventually no carbon residue was detected above 623 K. The TMA showed rapid weight decrease until the temperature reached 650 K, following a slow weight decrease appearing at 650-700 K.   Remaining carbon yield on TMA at 700 K was about 4.2 wt%.   The PG showed a gradual weight loss during entire heating process up to 1273 K with 36 wt% of carbon yield. A close examination indicated that main pyrolysis occurred in the temperature range of 500-650 K, following a gradual weight decrease above 650 K.

The interactions between PF and pore former produce significant may change in their individual thermal behavior. These changes are expected to reflect in difference between experimental and calculated curves. **Fig.2** shows the TG curves of the mixtures (PA/PF, TMA/PF, and PG/PF) and the corresponding calculated curves. The calculated curves are the lines that were obtained by assuming that there are no interactions operating at interface between PF and pore former. That is, PF and pore former are carbonized individually; therefore one can calculate the curves by knowing the weight ratio of PF and corresponding pore former.
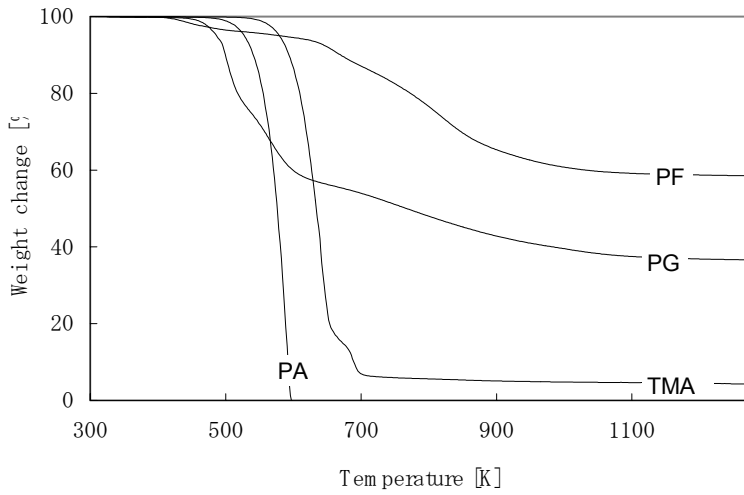
**Fig.1** TG curves of PF and pore formers (PA, TMA and PG)
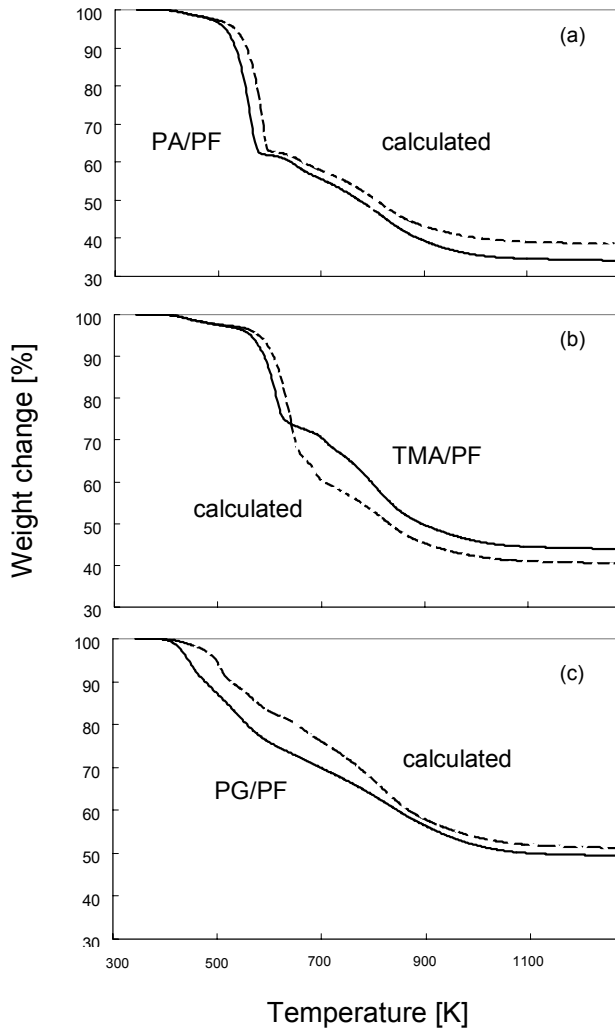
Fig.2 TG curves of PA/PF, TMA/PF, and PG/PF and their calculated TG curves

The results of TGA demonstrated that the PA/PF curve coincides practically with the calculated PA/PF curve at an entire temperature range up to 1273 K (**Figs.2a**). A similar observation is seen for TMA/PF to 650 K, however the carbon yield on TMA/PF experimental curve exceeds the calculated curve above 650 K (**Figs.2b**). It is inferred, therefore, that PA and TMA decomposed individually in PF matrix below 650 K. Above this temperature, TMA could have some interactions with PF in a way to increase the carbon yield. On the other hand, a noticeable difference in weight curves was detected by the comparison between PG/PF and calculated curves, especially at a temperature range of 400-900 K (**Fig.2 c**). This difference seems to be an indication that PG is being interacted with PF at their interfaces.

An obvious question arises concerning the nature of interaction between pore former and PF during their heat treatment. It is submitted that measurement of heat flow during carbonization answers, in part, how the interaction occurs. **Fig.3** shows DSC results on PF, three mixtures (PA/PF, TMA/PF, and PG/PF), and corresponding pore formers (PA, TMA and PG). **Fig.3a** presents the DSC data on PF, PA/PF, and PA heat treated up to 873 K at 5 K/min in flowing argon. A sharp endothermic peak was detected at 617 K for PA. This peak shifted slightly to a lower temperature of 610 K for PA/PF. It is seen in **Fig.3b** that the TMA showed a endothermic peak at 642 K, temperature of which is eventually same as that found for TMA/PF (642 K). However, an exothermic peak (719 K) found for TMA was shifted slightly to a lower temperature (704 K) with considerable reduction of the peak area when TMA was mixed with PF: TMA/PF. These observations, coupled with previous TG data, suggest that pore former of PA in PF matrix behaved thermally as if they were present as single component up to 1273 K, and that TMA in PF behaved in a similar way as found in PA. However, situation becomes more complex as the temperature increases above 650 K, showing some interactions between TMA and PF. An endothermic peak at 494 K was clearly detected in **Fig.3c**, which shows the DSC curves on PF, PG/PF, and PG. The PG. indicated a strong endothermic peak at 494 K. The addition of PG into PF leads to disappearance of this peak, or shift to a lower temperature of 456 K with a considerable small peak. This observation suggest that the carbonization behavior of PG/PF is being proceeded differently in a manner that PG pore former interacts, in some fashions, with PF matrix at their interface, emerging the interaction even at a lower temperature of about 450 K.

Three pore formers of PA, TMA and PG are used in this study; PA contains two carboxylic groups in a benzene ring, TMA with three carboxylic groups, and PG with three phenolic groups. Examination of TGA and DSC results indicates that effectiveness of interaction between pore former and PF at their interface is as follows: PG>TMA>PA. It is also suggested, from comparison between TMA and PG,

that phenolic group in pore formers interacted strongly with PF than carboxylic group does, thus changing the carbonization behavior during heating process of PF resin.
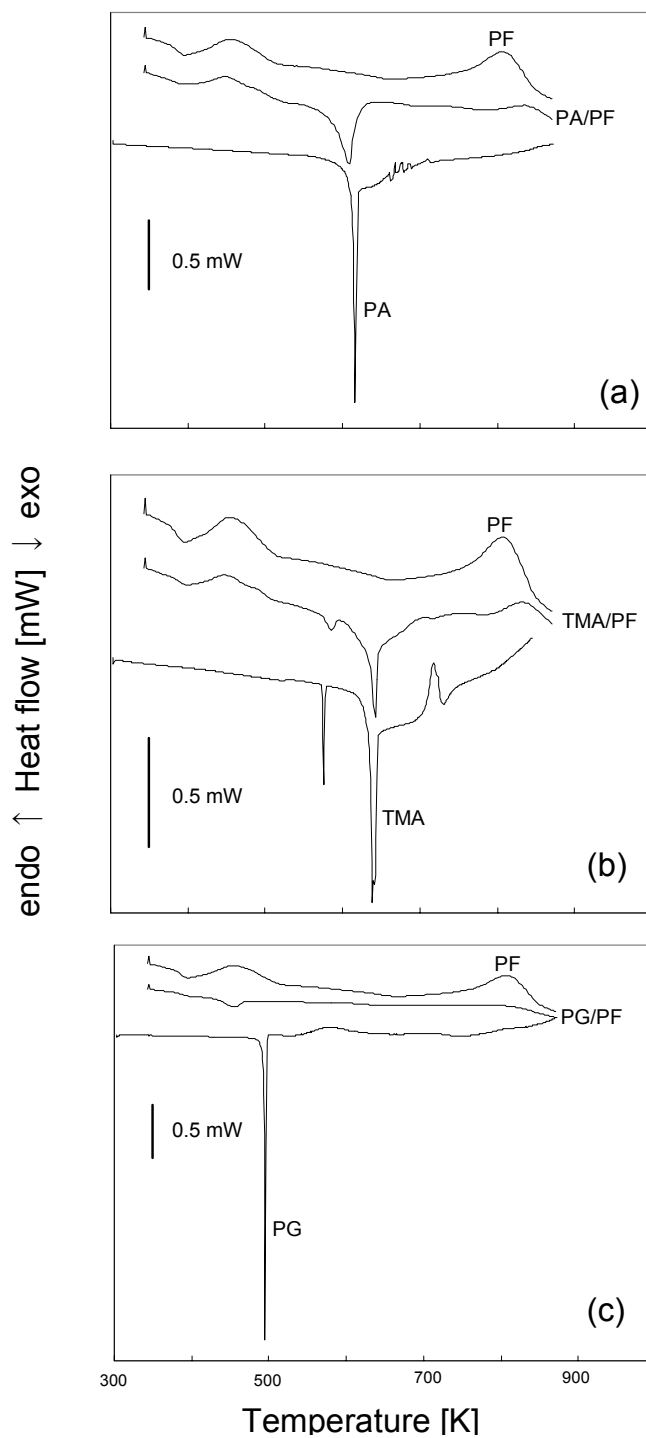
Fig.3 DSC curves of PF, PA/PF, TMA/PF, PG/PF mixtures and corresponding pore formers

4. Conclusion

The carbonization of phenol-formaldehyde resin (PF) and PF with m-phthalic acid (PA), trimesic acid (TMA) and phloroglucinol (PG) were carried out in order to study the interaction of PF and pore formers by use of thermogravimetric analysis (TG) and differential scanning calorimetry (DSC). Pore formers showed different interactions between PF (phenol-formaldehyde resin) and pore formers during their heating process, and these interactions were found to occur at different temperature range, depending on the type of pore formers added in PF. The PA had small interactions between PF during heat treatment. The TMA (trimesic acid) indicated an additional interaction above 650 K. The PG (phloroglucinol) had large interactions from a lower temperature, emerging around 450 K. It is suggested that phenolic group in pore formers interacted strongly with PF than carboxylic group does, thus changing the carbonization behavior during heating process of PF resin.

5. References

[1] Hatori, H., Yamada, Y., Shiraisi, M., Iimura, Y., and Kimura, T., Extended Abstr. Program Bienn Conf. Carbon, 22 (1995) 416-417

[2] Hatori, H., Kobayashi, T., Hanzawa, Y., Yamada, Y., Imamura, Y., Kimura, T., and Shiraisi, M., J.Appl.Polyu.Sci., 79 (2001) 836-841

[3] Takeichi, T., Yamazaki, Y., Fukui, K., Matsumoto, A., and Inagaki, M., Tanso, 195 (2000) 388-394

[4] Takeichi, T., Yamazaki, Y., Zuo, M., Ito, A., Matsumoto, A., and Inagaki, M., Carbon, 39 (2001) 257-265

[5] Oya, A., Nakahara, M., and Endo, N., Japanese Unexamined patent No.13223, (1997)

[6] Ozaki, J., Endo, N., Ohizumi, W., Igarashi, K., Nakahara, M., and Oya, A., Carbon, 35 (1997) 1031-1033

[7] Horie, Y., Shiraishi, S., and Oya, A., J.Matter.Sci.Let., 20 (2001) 105-106

[8] Ozaki, J., Ohizumi, W., and Oya, A., Carbon, 38 (2000) 1499-1524

[9] Horikawa, T., Ogawa, K., Mizuno, K., and Muroyama, K., Carbon, 41 (2003) 465-472

[10] Inomata, K., Bachelor thesis, Meiji University, 2004.