JOURNAL OF MATERIALS SCIENCE 24 (1989) 2781–2786

Morphology change in carbons prepared from pitch–polyvinylchloride mixtures under pressure

MICHIO INAGAKI, MASAYUKI URATA, MOTOTSUGU SAKAI
Materials Science, Toyohashi University of Technology, Tempaku-cho, Toyohashi, 440 Japan

Mixtures of fractionated pitches with different molecular weights and polyvinylchloride (PVC) were carbonized at 650° C under a pressure of 30 MPa. The morphology of the carbons obtained was studied under a scanning electron microscope and the optical texture under a polarized light microscope. Gradual changes in morphology are observed, from lump-type to coralloidal through botryoidal with gradual diminution in the size of the primary particles. The content of PVC and also the number-averaged molecular weight were found to govern the morpohology of the resultant carbon.

1. Introduction

In carbon materials, a variety of textures are found; microtexture which can be observed under a transmission electron microscope, optical texture which can be seen under a polarized light microscope, texture such as filler coke and carbon matrix derived from the binder pitch, etc. Each of these textures has been pointed out to have great importance to elucidate the properties of carbon materials.

Pitches are important raw materials for carbon industries, as binders for various electrographitized carbon materials and also as precursors for pitch-based carbon fibres. We have been studying the visco-elastic properties of pitches by introducing a fractionation technique [1–4]. Carbonization of the fractionated pitches showed different contributions of the fractions with different molecular weights to form the mesophase and consequently the texture of resultant carbons

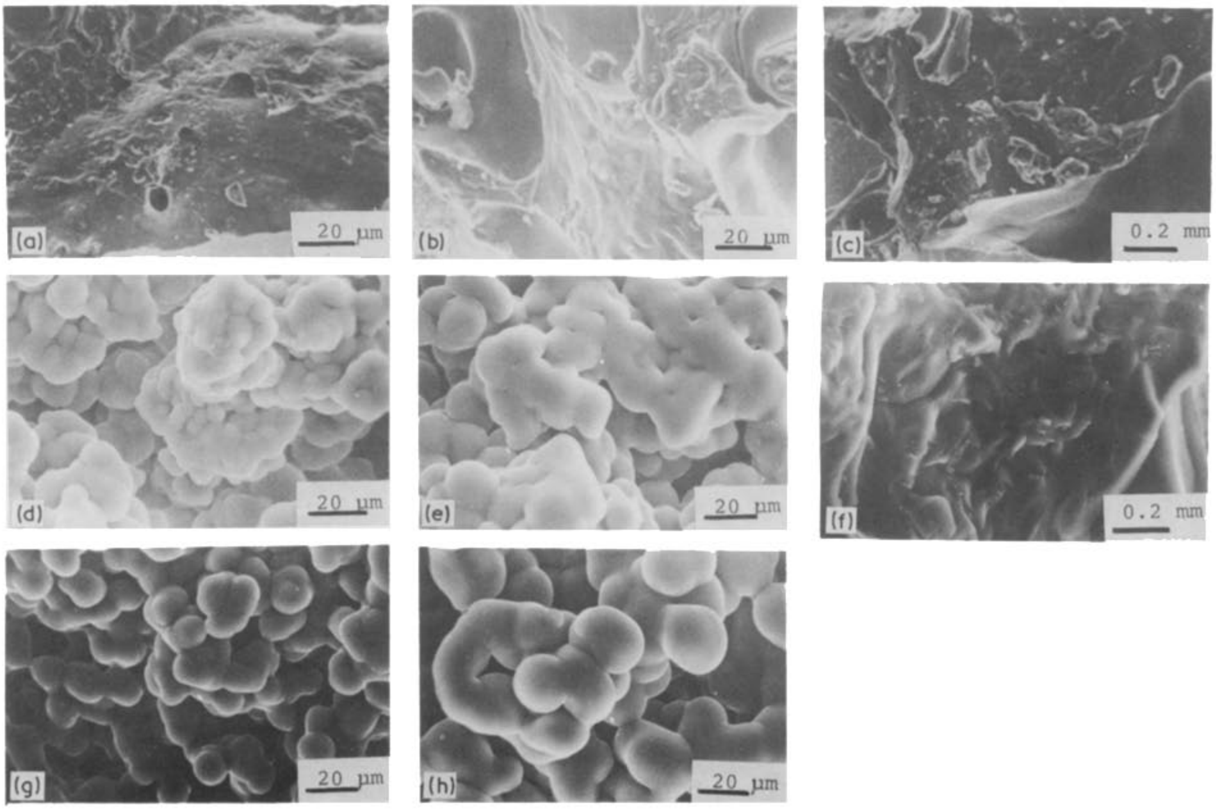

Figure 1 Morphology changes in carbons obtained from mixtures of fractionated pitches and PVC under a closed system of 30 MPa at 650° C. PVC content 0%: (a) PF-1, (b) PF-3, (c) PF-5. 10% PVC: (d) PF-1, (e) PF-3, (f) PF-5. 30% PVC: (g) PF-1, (h) PF-3. 50% PVC: (i) PF-1, (j) PF-3, (k) PF-5. 60% PVC: (l) PF-1, (m) PF-3, (n) PF-5. 70% PVC: (o) PF-1, (p) PF-3, (q) PF-5. 90% PVC: (r) PF-1, (s) PF-3, (t) PF-5.

0022–2461/89 $03.00 + .12

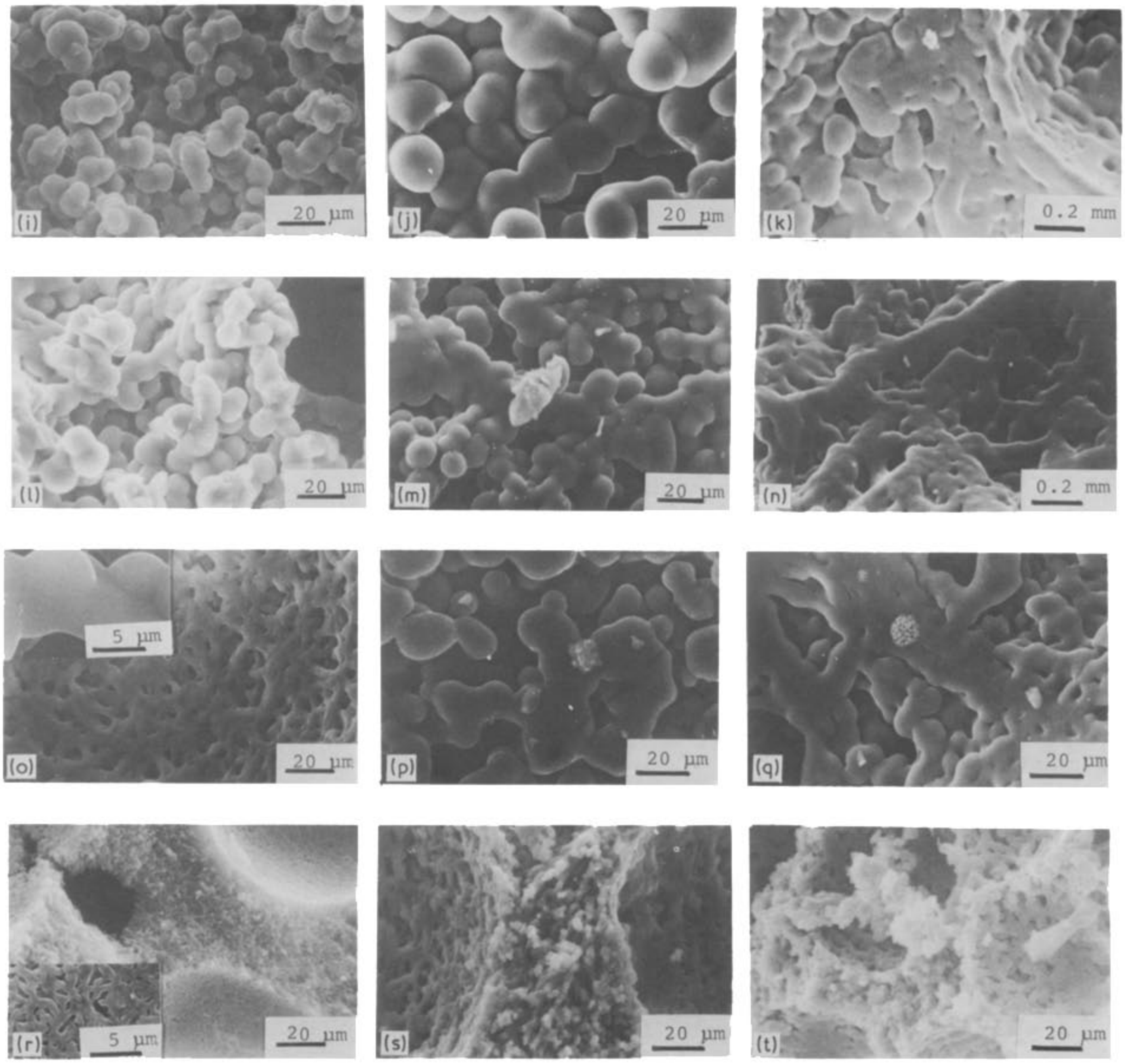

Figure 1 Continued

[5, 6]. We have used a pressure carbonization process which gives a high carbon yield and interesting texture and morphology in carbons [5–13]. Also we tried to modify the optical texture of carbons by mixing either phenol resin or polyethyleneterephthalate (PET) to pitches [11, 12, 14, 15].

In the present work, mixtures of pitch and polyvinylchloride (PVC) are carbonized under pressure, and the resultant carbons are observed under scanning electron and polarized light microscopes.

2. Experimental procedure

The original pitch, Ashland 240, was fractionated by using combinations of a good solvent (benzene) and a poor solvent (n-hexane) according to the procedure reported before [1]. The number-averaged molecular weight of each benzene-soluble fraction is shown in Table I. Each fraction was recovered as a powder with a size of a few micrometres. The PVC used was a powder with a size of 20 to 50 μm. For carbonization with PVC, the fractions PF-1, PF-3 and PF-5 were selected in order to cover a wide range of molecular weight of pitches. Two materials, fractionated pitch and PVC in fine powders, were mixed in different weight ratios by suspending both in methanol. After mixing, methanol was vaporized out at room temperature.

Carbonization was carried out at 650° C for 1 h under a pressure of 30 MPa in a Stellite bomb by keeping samples either in a sealed gold tube or in an open gold tube (7 mm in diameter, 50 mm long and 0.1 mm thick). The carbonization yield from each fraction of pitch is summarized in Table I in two cases under the closed or open system of gold tube. The

TABLE I Number-averaged molecular weight of benzene-soluble fractions of a pitch and their carbonization yield under 30 MPa at 650° C.

Fraction	Number-averaged molecular weight	Carbonization yield (wt %)	
		Closed system	Open system
PF-1	380	87	67
PF-2	450	89	78
PF-3	590	89	82
PF-4	750	89	84
PF-5	910	89	87

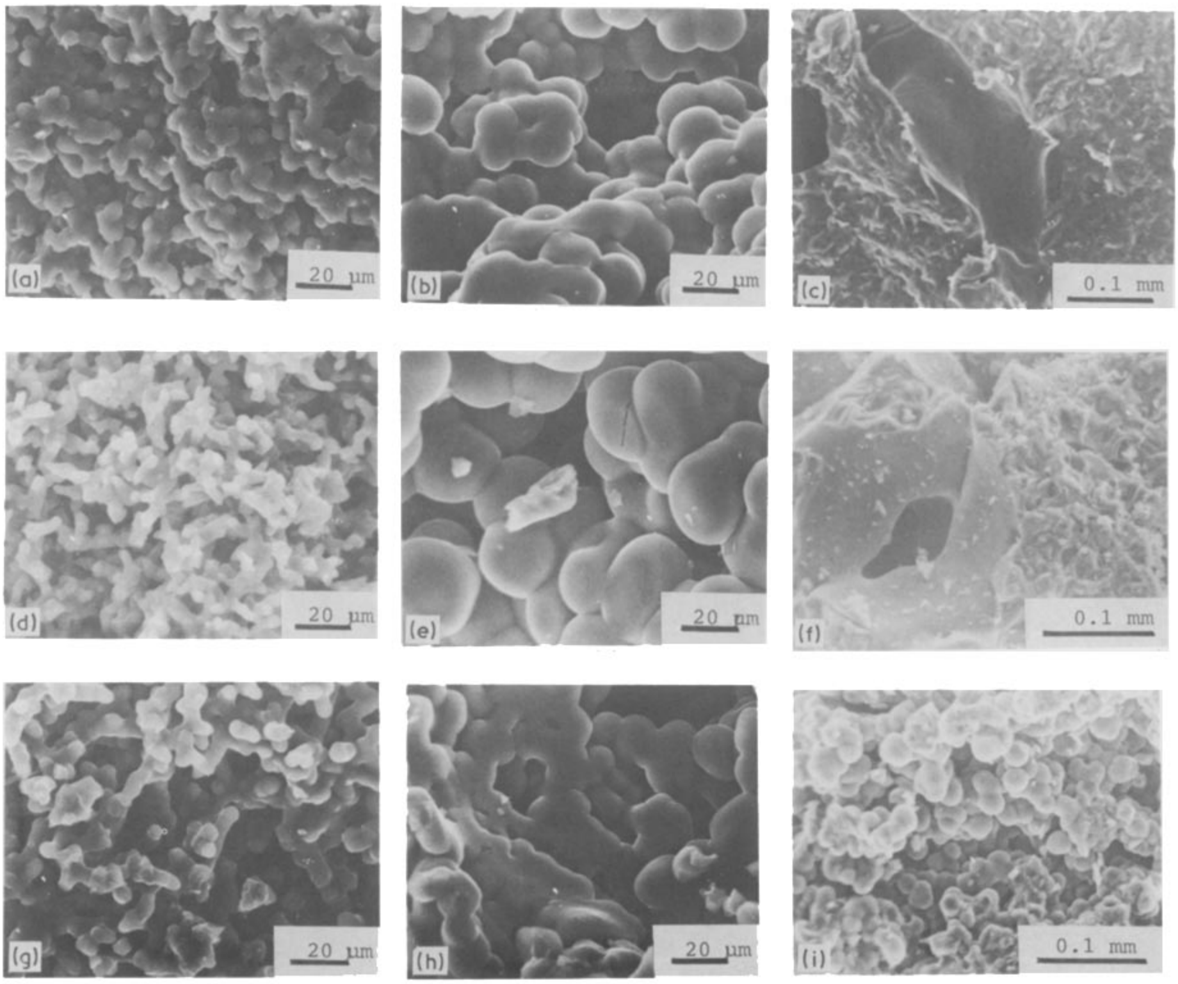

Figure 2 Morphology changes in carbons obtained from mixtures of fractionated pitches and PVC under an open system of 30 MPa at 650° C. 10% PVC: (a) PF-1, (b) PF-3, (c) PF-5. 30% PVC: (d) PF-1, (e) PF-3, (f) PF-5. 50% PVC: (g) PF-1, (h) PF-3, (i) PF-5. 60% PVC: (j) PF-1, (k) PF-5. 70% PVC: (l) PF-1, (m) PF-3, (n) PF-5. 90% PVC: (o) PF-1, (p) PF-3, (q) PF-5.

detailed procedure for carbonization is exactly the same as reported before.

The resultant carbons were observed under a scanning electron microscope and then under a polarized light microscope after polishing their cross-section.

3. Experimental results

The morphology changes with content of PVC in starting samples are summarized in Fig. 1 for the carbons obtained under the closed system and in Fig. 2 for those under the open system. Polarized light micrographs of some carbons are shown in Fig. 3.

The general trend of morphology change with addition of PVC in the resultant carbon is seen in the fraction PF-1 under the closed system. From pure PF-1, coke lumps which do not have any characteristic morphology are obtained (Fig. 1), and a coarse mosaic optical texture (Fig. 3) is obtained. By the addition of PVC, however, a remarkable change in the morphology is observed: a botryoidal morphology and a gradual decrease in the size of its primary particles. The size of the primary particles decreases from about 20 µm to about 10 µm with an increase in PVC content from 10 to 60%. These particles have an anisotropic optical texture and seem to be coalesced; it is difficult to find particles with the Brooks–Taylor type of mesophase texture. Above 70% PVC the primary particles become remarkably small and elongated. By the addition of 90% PVC, the carbon obtained looks like connected strings with a diameter less than 1 µm. Its appearance is similar to a kind of coral, so we call it coralloidal. Its optical texture is difficult to determine because of its small size, but it seems to be anisotropic.

On the fraction PF-3 which has a slightly larger average molecular weight, the same change in morphology is observed. Up to 70% PVC, relatively large particles are observed and from the mixture of 90% PVC the carbon with coralloidal morphology is obtained.

On the fraction PF-5 which has the highest molecular weight of the benzene-soluble fractions, the morphology change shifts to a higher PVC content. In order to obtain carbons with a botryoidal morphology the addition of PVC up to 60 to 70% is needed. The carbon from 90% PVC, however, is coralloidal.

Under the open system the same morphology change, from lump-type to botryoidal and then to coralloidal, is observed (Fig. 2). For the fraction PF-1, only 10% addition of PVC is enough to change the morphology to botryoidal, but the size of the primary particles is about 5 µm, much smaller than that under the closed system. The size of the primary particles becomes comparable with that obtained under the

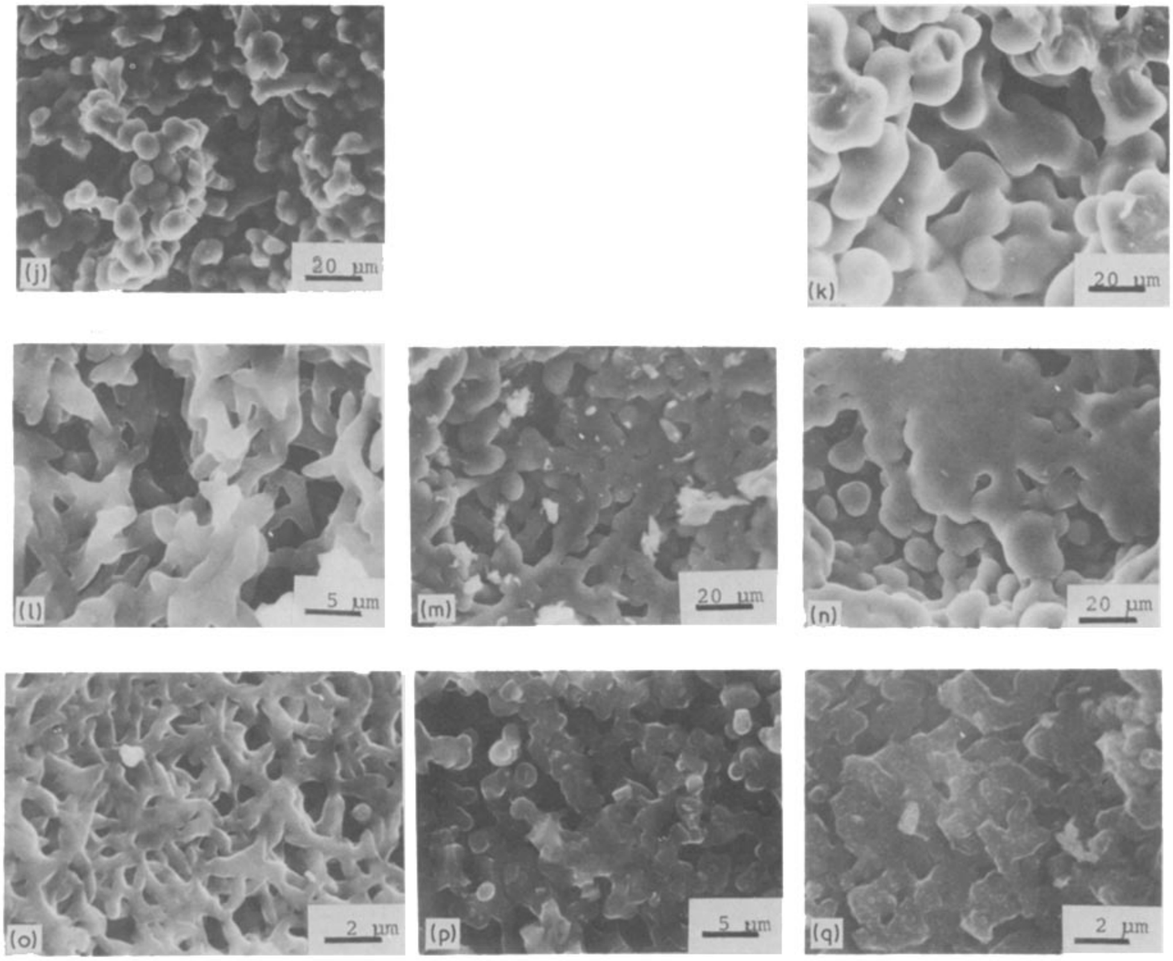

Figure 2 Continued

closed system above 50% PVC. Above 70% the primary particles becomes much smaller and the morphology can be called coralloidal. In the carbon obtained from the 60% PVC sample, material with a coralloidal morphology was partly found. On the carbons obtained from the fractions PF-3 and PF-5, the morphology changes with PVC content are found to be very similar to those found under the closed system; for the fraction PF-3, botryoidal with 10 to 20 μm particles up to 70% and coralloidal at 90% PVC, and for PF-5, lumpy up to 50%, botryoidal at 60 to 70% and then coralloidal above 80% PVC.

In Fig. 4, the carbonization yields from different fractions are plotted as a function of PVC content. In every system the yield decreases linearly with increase in PVC content. Except for the fraction PF-1, the yield values are not much different among the fractions used. Under the open system the fraction PF-1 on its own gives a low yield, and so to reach the yield values of the closed system more than 50% of PVC has to be added.

4. Discussion

By using fractionated pitches with different molecular weights, we observed interesting morphology changes in the carbons obtained under pressure with PVC content, from lump-type in the usual cokes to coralloidal through botryoidal, associated with a size diminution of the primary particles. In Fig. 5, these morphology changes are schematically illustrated as functions of the number-averaged molecular weight and content of PVC. The transitions from lump-type to botryoidal and also from botryoidal to coralloidal morphology are not clear-cut, but gradual with the size diminution of particles. If the primary particles are too large to differentiate and are coalesced with each other, it looks lumpy. With decreasing particle size the lumps show a smoothly rugged surface, as seen in Fig. 1 on the carbon obtained from the fraction PF-5 with 60% PVC. If the particles become less than 20 μm, the morphology of the carbon is called botryoidal, as shown in Figs 1 and 2; if the particles become too small, roughly less than 1 μm, we obtain a coralloidal morphology where it is difficult to recognize particles again.

As has been shown in Figs 1 and 2 by SEM micrographs and summarized schematically in Fig. 5, the morphology change depends on the molecular weight of the pitch component. A pitch with a high molecular weight (PF-5) needs a large amount of PVC in order to modify the morphology from its natural lump-type to botryoidal. From a low molecular weight pitch (PF-1), a botryoidal morphology of carbon is obtained by a small addition of PVC, though the pitch itself gives a lump-type morphology. In other words, PVC works effectively in a low molecular weight pitch to reduce the size of the primary particles.

Under the open system a low molecular weight

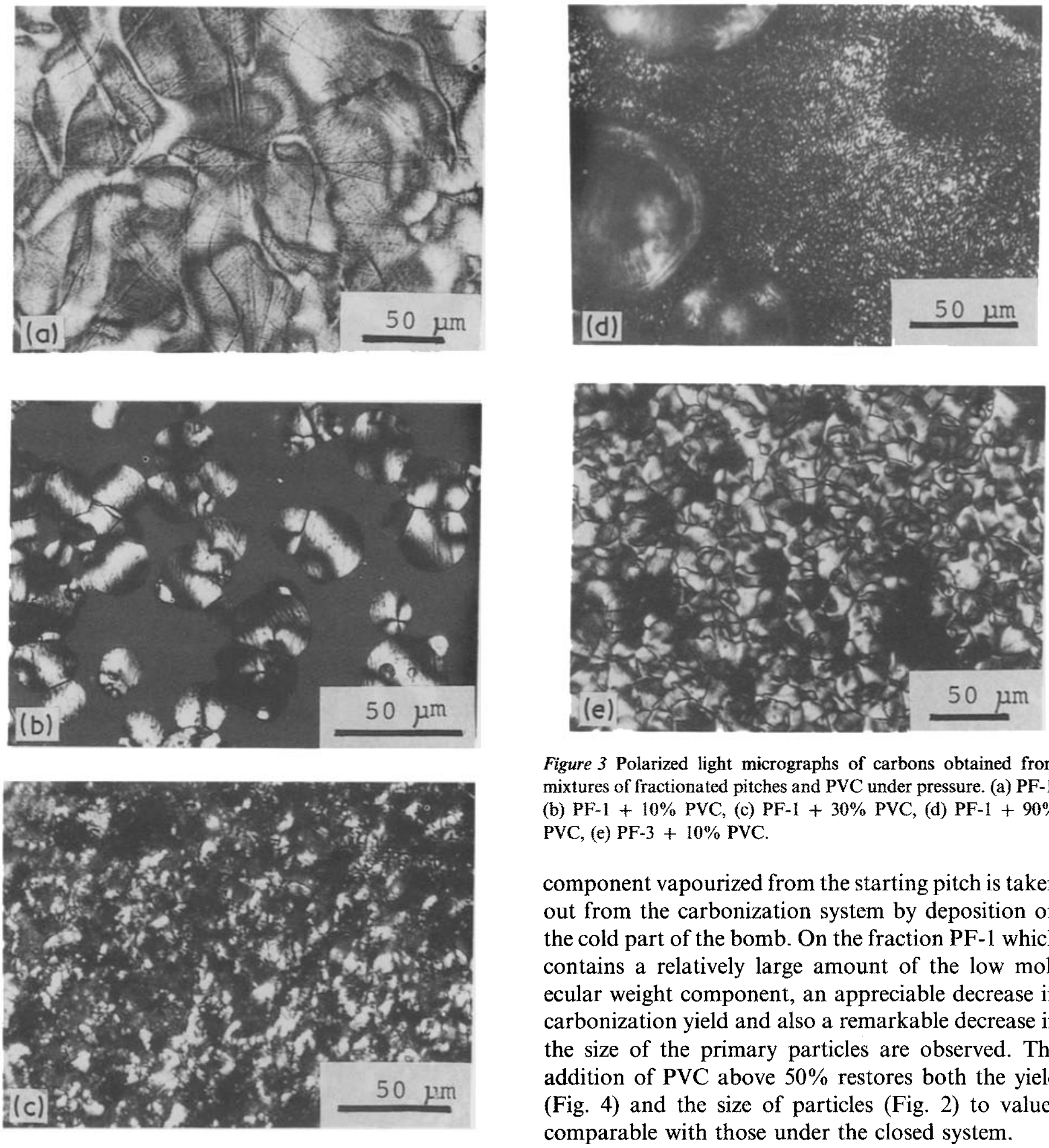

Figure 3 Polarized light micrographs of carbons obtained from mixtures of fractionated pitches and PVC under pressure. (a) PF-1, (b) PF-1 + 10% PVC, (c) PF-1 + 30% PVC, (d) PF-1 + 90% PVC, (e) PF-3 + 10% PVC.

component vapourized from the starting pitch is taken out from the carbonization system by deposition on the cold part of the bomb. On the fraction PF-1 which contains a relatively large amount of the low molecular weight component, an appreciable decrease in carbonization yield and also a remarkable decrease in the size of the primary particles are observed. The addition of PVC above 50% restores both the yield (Fig. 4) and the size of particles (Fig. 2) to values comparable with those under the closed system.

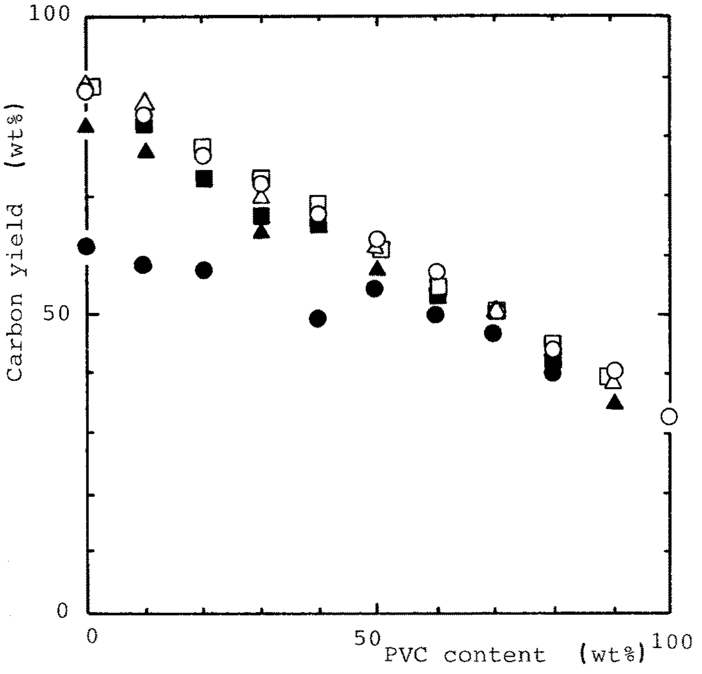

Figure 4 Carbon yield after carbonization under 30 MPa at 650° C for 1 h against PVC content in fractionated pitches. Closed system: (○) PF-1, (△) PF-3, (□) PF-5, (●) PF-1, (▲) PF-3, (■) PF-5.

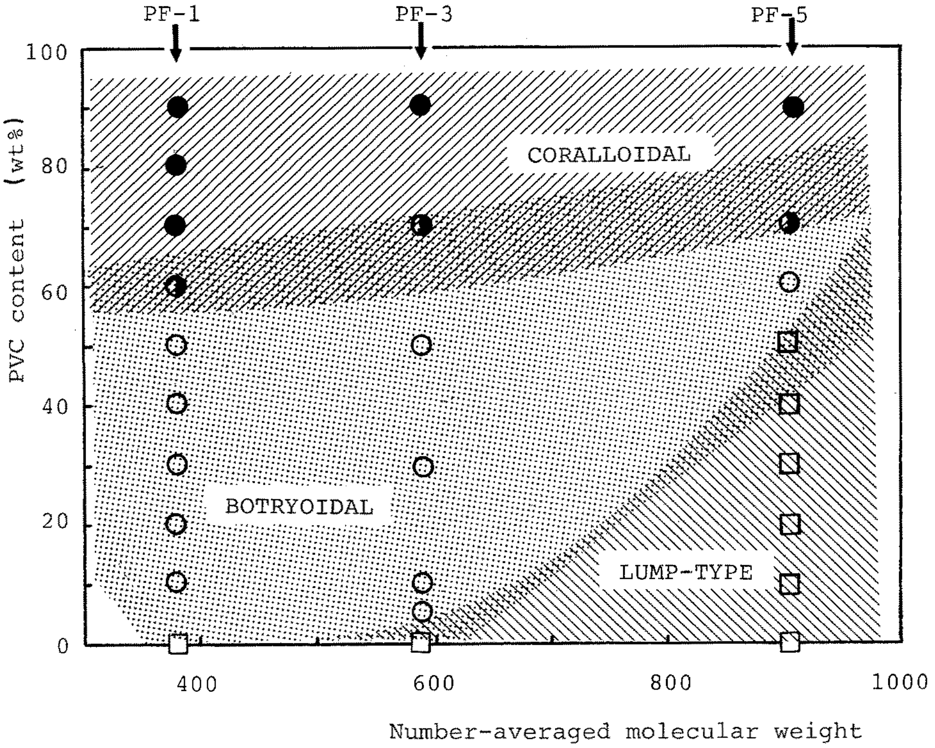

Figure 5 Morphology changes with number-averaged molecular weight of pitch and content of PVC.

By pressure carbonization of mixtures of polyethylene (PE) with PVC, we have obtained separate single spherules with a uniform size [8–10]. It has been pointed out that the coexistence of two components is essential to form single spherules: one is the hydrocarbon component, which is formed mainly from PE and has a molecular weight low enough to vaporize out under normal pressure, and the other is a functional component which is formed by the thermal decomposition of PVC at relatively low temperatures and seems to carry some radicals. The ratio between these two components is very important to obtain separate carbon spherules and can be controlled by mixing either component [13]. Carbons with a botryoidal morphology are obtained on each side of the ratios giving spherules.

In the present work single spherules are not obtained, probably because the ratio between the above-mentioned two components is out of the range to give single spherules. Even for the morphology containing coalesced particles, however, remarkable effects of the addition of PVC and also the molecular weight of pitch are observed. Therefore the morphology of carbons obtained under pressure has to be discussed on the bases of the ratio between functional and hydrocarbon components, and also of the molecular weight of the latter. To examine this we have to find suitable precursors of which the molecular weight is uniform and also can be controlled over a wide range.

References

1. M. SAKAI and M. INAGAKI, *Carbon* **19** (1981) 37.
2. M. SAKAI, K. SASAKI and M. INAGAKI, *ibid.* **21** (1983) 593.
3. M. SAKAI, T. SOGABE, H. KITAGAWA and M. INAGAKI, *ibid.* **21** (1983) 601.
4. M. SAKAI, T. KIDA and M. INAGAKI, *J. Mater. Sci.* **19** (1984) 2651.
5. M. INAGAKI, K. KURODA, M. SAKAI, E. YASUDA and S. KIMURA, *Carbon* **22** (1984) 335.
6. M. INAGAKI, K. GOTO and M. SAKAI, *TANSO* No. 126 (1986) 110.
7. M. INAGAKI, M. ISHIHARA and S. NAKA, *High Temp.-High Press.* **8** (1976) 279.
8. M. INAGAKI, K. KURODA and M. SAKAI, *ibid.* **13** (1981) 207.
9. *Idem, Carbon* **21** (1983) 231.
10. M. INAGAKI, K. KURODA, N. INOUE and M. SAKAI, *ibid.* **22** (1984) 617.
11. I. OGAWA, H. YOSHIDA, K. KOBAYASHI and M. INAGAKI, *J. Mater. Sci.* **20** (1985) 414.
12. M. INAGAKI, M. WASHIYAMA and M. SAKAI, *Carbon* **26** (1988) 169.
13. M. WASHIYAMA, M. SAKAI and M. INAGAKI, *ibid.* **26** (1988) 303.
14. I. OGAWA, M. SAKAI and M. INAGAKI, *Yogyo Kyokai Shi* **91** (1983) 456.
15. *Idem, J. Mater. Sci.* **20** (1985) 17.

Received 20 October 1987
and accepted 17 February 1988