Texture control of carbons by mixing polyethyleneterephthalate into pitch

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Mixtures of pitch and polyethyleneterephthalate (PET) powders were carbonized in a gold tube under various pressures. Carbon yields, optical textures and the process of formation and growth of mesophase were studied. The carbon yields gradually decreased with an increase in PET content. By carbonization under normal pressure, only 10 to 20 wt% of PET was effective to obtain a homogeneous optical texture of fine mosaic type. Under a pressure of 30 MPa, carbon with a fine mosaic texture was found in a larger range of PET content of 30 to 50 wt% with a high carbon yield. The nucleation of mesophase in the pitch–PET system at 450° C under 5 MPa was more rapid and larger in number than in the pitch alone.

1. Introduction
The texture of carbon materials governs their high-temperature behaviour and principal properties, and so a great deal of effort has been devoted to control and design of the texture of carbons. The microtexture observed under a high-resolution electron microscope determines the graphitization behaviour of carbons [1]. The formation and growth of mesophase in pitches and the texture of bulk mesophase govern the texture and properties of the resultant carbons, cokes and fibres, and so are very important for subsequent manufacturing processes [2].

We have been trying the control of mesophase texture, and consequently the texture of carbons, by mixing two different kinds of carbon precursor and carbonizing under pressure. When powder mixtures of polyethylene, polypropylene and polystyrene with small amounts of polyvinylchloride and polyvinylidenechloride were carbonized under pressures above 10 MPa, carbon spherules were obtained with a homogeneous size of 2.5 to 0.5 μm and with a radial arrangement of carbon layers [3–6]. The conditions for the formation of spherules were discussed [6]. Under pressure, the formation in a pitch of mesophase spheres with a high concentration, much higher than under normal pressure, and with a homogeneous size was reported [7]. Mixtures of pitch and phenolic resin by using a solvent were found to give a homogeneous texture of the resultant carbons [8–10], which changed gradually from a coarse mosaic type to isotropic through fine mosaic on increasing the content

of phenolic resin. A combination of a coal extract and an industrial resin was reported to give carbon with a fine mosaic texture under pressure [11].

In the present work, the addition of polyethyleneterephthalate (PET) to pitch was found to be very effective to control the optical texture of the resultant carbons, of which the domain size depended strongly on the content of PET and the carbonization conditions.

2. Experimental procedure
A benzene-soluble part was recovered as a fine powder from a benzene solution of petroleum pitch (Ashland 240) by the freeze-drying method. A powder of PET with diameter under 150 μm was prepared by sieving. Mechanical mixtures of these two raw materials in various ratios were placed in a thin-walled gold tube (7 mm in diameter, 50 mm long and 0.1 mm thick) and sealed in after replacing the air inside the tube by argon. By using an autoclave the gold tube was heated up to various temperatures under various pressures for 1 or 5 h (closed system under pressure). Mixtures of pitch and PET were also heated in the same way under normal pressure after being sealed in the tube (closed system under normal pressure) and without sealing (open system under normal pressure). The experimental conditions are summarized in Table I. The heating rate was kept constant at 5° C min^{-1}. The sample mixtures were kept in the homogeneous temperature region of the furnace. The detailed experimental procedures have been reported previously [7].

TABLE I Conditions for carbonization

Carbonization system	Pressure (MPa)	Temperature (°C)	Soaking time (h)
Under pressure, closed system	5 to 30	500 to 650	1 to 5
Normal pressure, closed system	–	650	5
Normal pressure, open system	–	650	5
Under pressure, closed system	5	450	1 to 25
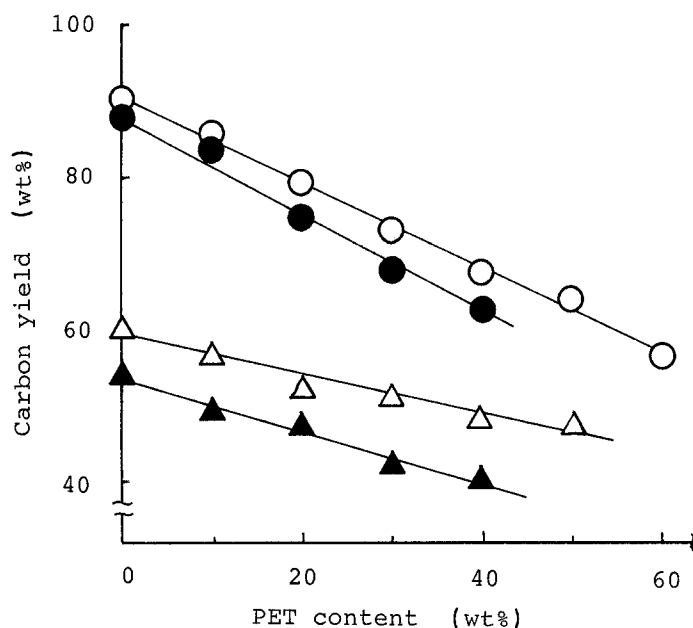
The yield of carbonaceous solids from the mixture was determined from the change in weight before and after carbonization. The optical texture of the carbons obtained was examined on polished cross-sections under a polarized-light microscope.

The process of formation of mesophase spheres and their coalescence was followed by observing the optical texture of the cross-section of the carbonaceous solids obtained in the closed system under 5 MPa at 450°C for 1 to 25 h (Table I).

3. Results and discussion
3.1. Carbon yield
The carbonization of the sample mixtures, as detected by a weight decrease, started around 450°C and the yield of carbonaceous residues decreased with an increase in temperature. The change in yield became small above 600°C and further heat treatment of the carbon residue obtained at 650 and 1000°C in a nitrogen atmosphere gave only a small weight decrease; for example, pitch + 10 wt % PET gave yields of 85 and 83% after carbonization at 600 and 650°C, respectively, for 5 h under 30 MPa, and the latter showed only 5% weight loss after heat treatment at 1000°C for 1 h (final carbon yield after 1000°C treatment was 81%). Therefore, the carbon yields after carbonization at 650°C were compared under different experimental conditions.

In Fig. 1, the changes of carbon yield are shown as a function of PET content under various conditions of carbonization. The carbon yields decrease linearly with an increase in PET content. High yield values are obtained at any content of PET in a closed system under 30 MPa in comparison with other systems, probably due to the effective conversion of low molecular weight components to carbon residues. Above a pressure of 10 MPa, almost the same yield values as those under a pressure of 30 MPa were obtained. Carbonization under pressure has been reported to give high yields of carbon [4, 7, 10, 12]. In the open system under normal pressure, a decrease in carbon yield from that in the closed system under normal pressure was observed. The decrement in carbon yield is due to the exclusion of volatilized low molecular weight components by deposition in the low-temperature part of the autoclave.

3.2. Optical texture
Polarized-light micrographs in Fig. 2 show the change in optical texture of the resultant carbons with PET content, from coarse mosaic for a low content of PET to isotropic for a high content through fine mosaic for the intermediate, in the closed system under a pressure of 30 MPa at 650°C. No apparent difference in optical texture was detected between the carbons obtained after 1 and 5 h at 650°C under 30 MPa.

In Fig. 3, the changes in optical texture observed in the carbons obtained under various conditions are summarized as a function of PET content. Here the optical textures are described in terms of coarse mosaic, medium mosaic, fine mosaic and isotropic, corresponding to the sizes of optical mosaic units of > 100, 100 to 10, < 10 μm and optically inactive, respectively.

Under a pressure of 30 MPa, the optical texture changes from the coarse flow type to isotropic in a relatively narrow range of PET content, from 30 to 50 wt %. In this range, however, the size of the mosaic unit decreases gradually with an increase in PET content, as can be seen in Fig. 2. The PET content at which medium and fine mosaic textures are observed decreases with a decrease in pressure of the carbonization.

Under pressures less than 10 MPa, including normal pressure, only 10 wt % addition of PET to the pitch reduces the size of the optical mosaic unit and 50 wt % is enough to make the carbon isotropic. The results under normal pressure in the closed system are similar to those under 5 MPa, but different from those in the open system. This is probably due to the fact that the pressure inside the closed gold tube has become a little higher than the normal pressure.

In the mixture with a constant PET content, the size of optical unit of the mosaic tends to become larger
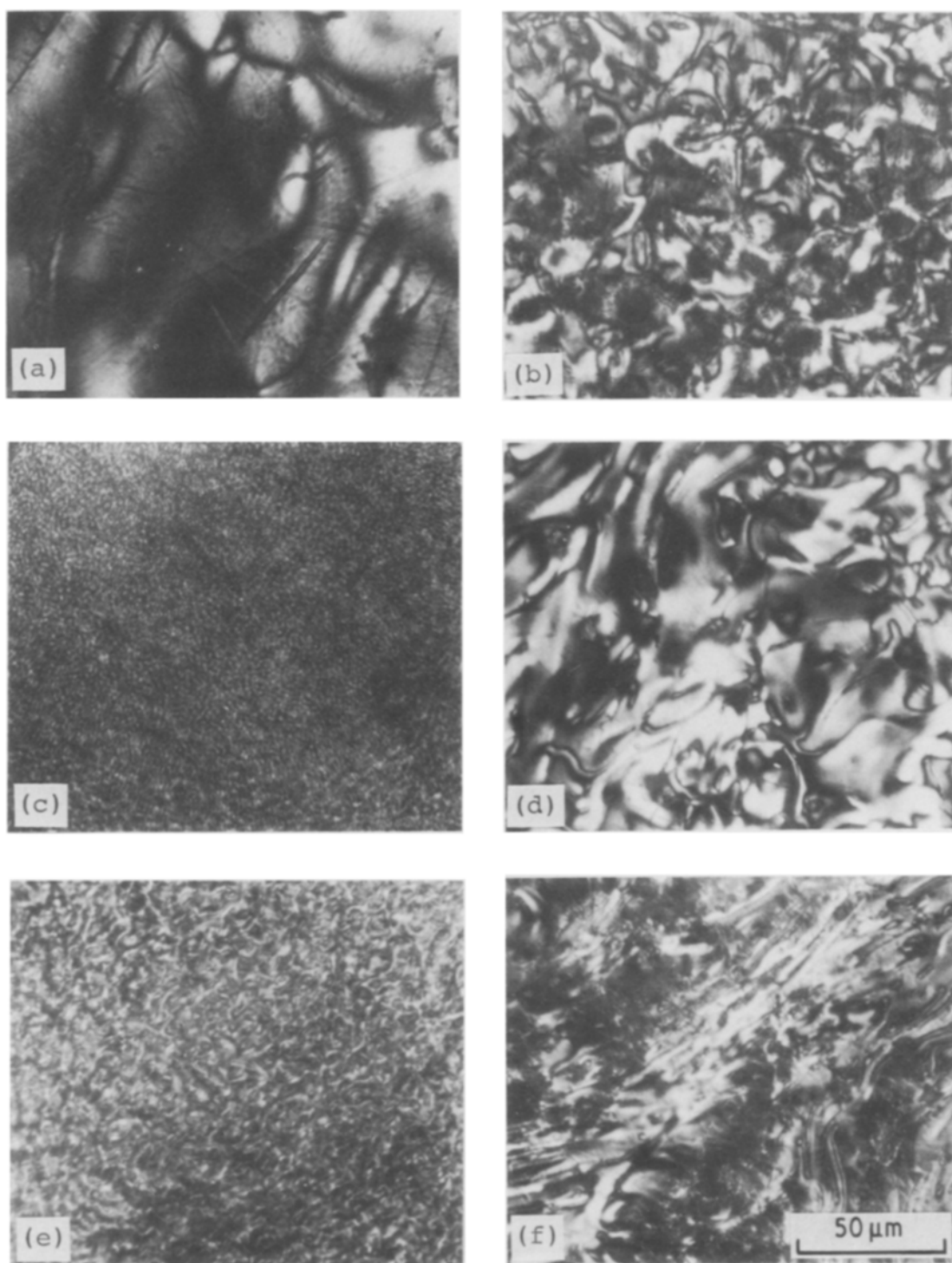
Figure 2 Polarized-light micrographs of the carbons obtained under various conditions. Under pressure, closed system: (a) 10, (b) 30, (c) 50 wt % PET. Normal pressure, closed system: (d) 20, (e) 30 wt % PET. Normal pressure, open system: (f) 20 wt % PET.

under higher pressures. This is presumed to be related to the suppression of volatilization of low molecular weight components, as discussed in the last section. The incorporation of low molecular weight components under pressure in a closed system may increase the fluidity of the viscous carbonaceous residues, and also may retard the growth of mesophase and the carbonization reactions.

3.3. Nucleation and growth of mesophase
In order to understand how the fine mosaic texture was formed in the pitch–PET system, the nucleation and growth of mesophase under 5 MPa at 450° C was

studied on the pitch–PET mixtures with 10 to 30 % PET as well as the pitch alone.

In Fig. 4, representative polarized-light micrographs are shown on the pitch + 30 wt % PET mixture and on the pitch itself as a function of soaking time at 450° C. After 1 h, both the pitch itself and the pitch–PET mixture gave an isotropic texture, no formation of mesophase spheres being observed. However, small numbers of anisotropic needle-like particles are detected in the pitch–PET system, which seem to be dispersed PET particles (Fig. 4a). Even when a large particle of PET was mixed into the pitch, it disappeared after heating up to 450° C and small
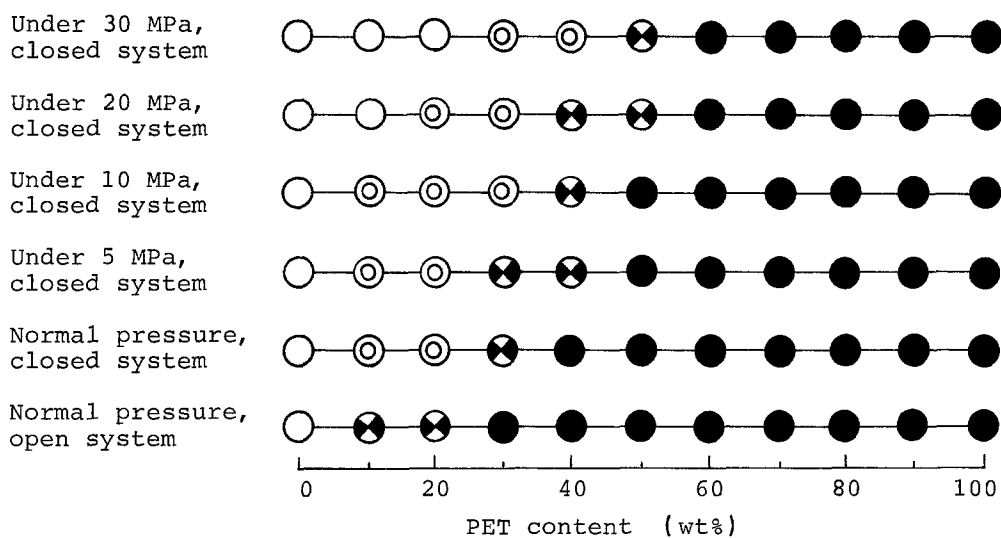
Figure 3 Optical texture of the resultant carbons under various carbonization conditions. (O) Coarse mosaic, (◎) medium mosaic, (⊖) fine mosaic, (●) isotropic.

needle-like particles were dispersed in the pitch matrix. After 5 h, a few mesophase spheres are observed in the pitch alone, but a larger number of small mesophase spheres in the pitch–PET system, although they are so small that we cannot actually say whether they are spheres or not (Fig. 4c). Here, we have to note that the size of the mesophase unit is quite different in the pitch itself and in the pitch–PET system. After 10 h, the difference becomes more remarkable. In the pitch the

size of spheres grows and most of them are single spheres. In the pitch–PET system, however, the number of spheres grows and many of them make contact with each other, but coalescence over a wide range is not detectable. In the pitch, after 15 h (Fig. 4f) almost all spheres started to coalesce with neighbouring spheres and the bulk mesophase texture partly appears. The coarse flow mosaic texture was established after 25 h. In the pitch–PET system, on the other
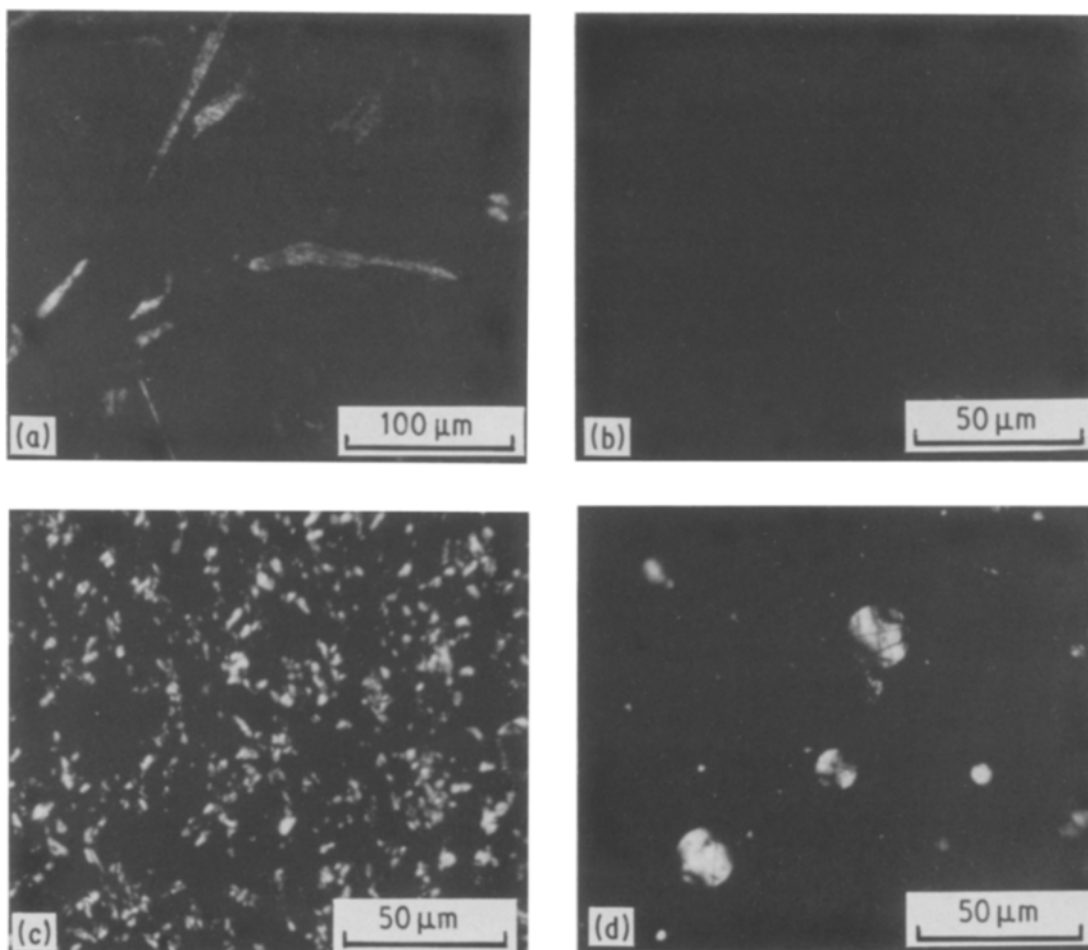

Figure 4 Polarized-light micrographs showing nucleation and growth of mesophase: (a, c, e, g) in the pitch–PET system, and (b, d, f, h) in the pitch alone, at 450° C under 5 MPa. (a, b) After 1 h; (c, d) 5 h; (e, f) 15 h; (g, h) 20 h.
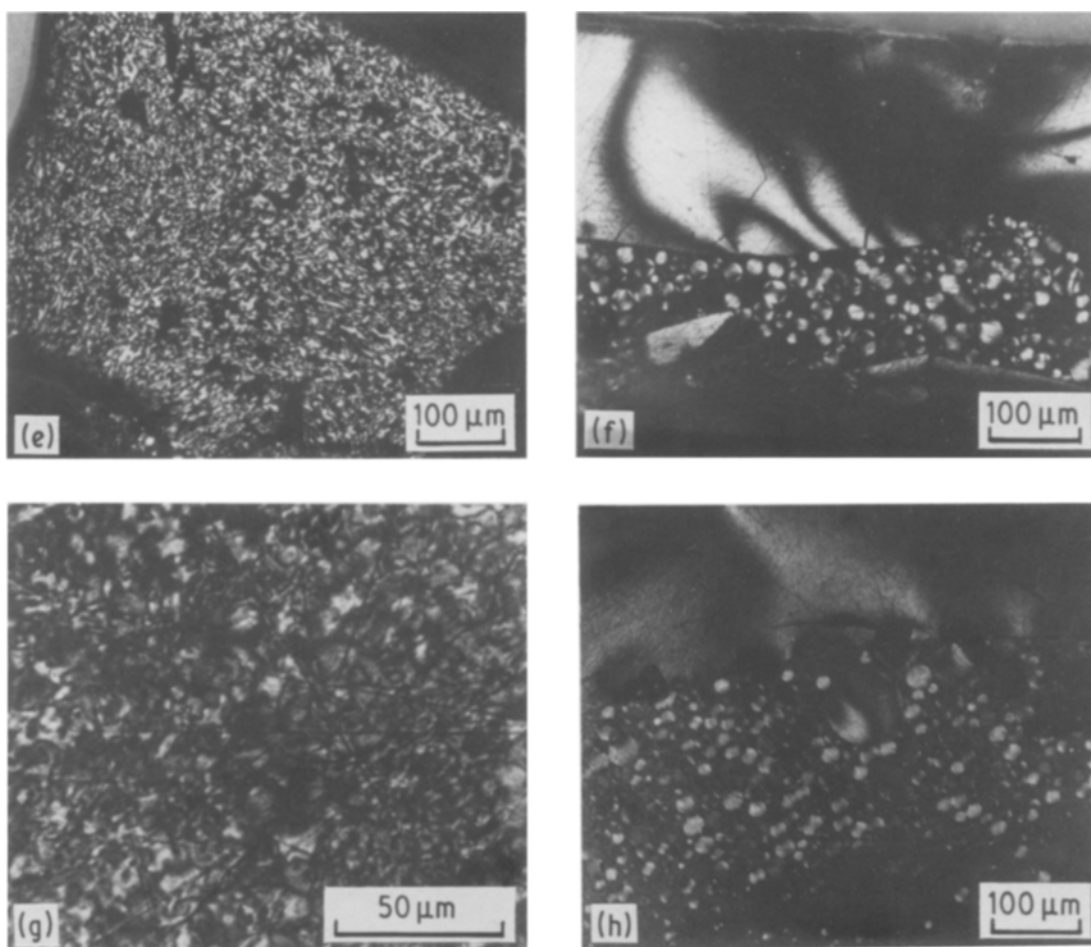
Figure 4 Continued.

hand, the fine mosaic texture is formed already after 15 h and the isotropic matrix is difficult to find (Fig. 4e).

In Fig. 5 the yields of carbonaceous residues in those two systems are plotted against soaking time at 450°C under 5 MPa, with short descriptions of the optical texture. In the pitch–PET system, the decrement of the yield of carbonaceous residues is very rapid until 10 h. Since the nucleation and growth of

mesophase, as shown in Fig. 4, occur in this range of soaking time at 450°C, depolymerized fragments of PET seem to be rapidly produced which are distributed in the pitch to act as nuclei of mesophase and to give a fine mosaic texture. The yield of carbonaceous residues becomes lower because the low molecular components are higher in concentration in comparison with the pitch itself. In the case of the pitch itself, on the other hand, the yield decreases gradually
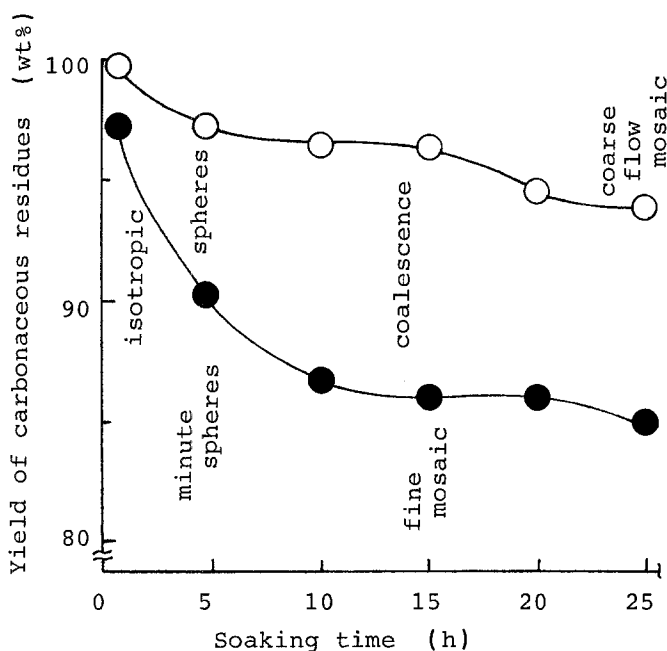

Figure 5 Yield of carbonaceous residues in (O) the pitch and (●) the pitch–30 wt % PET system at 450°C under 5 MPa.

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with soaking time, since the formation of the low molecular weight components is slow and they are low in concentration. As a result, the carbon yield becomes higher, and the nucleation, growth and coalescence of mesophase proceed gradually to give a coarse flow mosaic texture.

From these observations, the nucleation is so large in number and so rapid that no detectable coalescence occurs by the addition of PET. Consequently, carbon with a fine mosaic texture can be obtained with the addition of a small amount of PET.

4. Conclusions

The mixing of PET with pitch was found to reduce the size of mosaic units in the resultant carbons. In order to obtain a fine mosaic texture, only 10 wt % of added PET is enough in the open system under normal pressure, but 50 wt % of PET has to be added in the closed system under 30 MPa. However, the open system yields relatively low carbon residues and carbonization in the closed system under pressure is desirable because of the high carbon yield. From these points of view, the formation of fine mosaic texture and high carbon yield, carbonization under 5 MPa with the addition of 10 to 30 wt % of PET seems to be optimum.

The addition of PET to pitch in order to control the mesophase texture has advantages in the following two points: the small amount of additives and also the mechanical mixing of powders. In the case of phenolic resins, large amounts of additives (50 to 60 wt %) and either mixing by using a solvent (such as pyridine) or selecting a special combination of pitch and resin were necessary for obtaining a fine mosaic texture in the resultant carbons [8, 10, 11].

The present results can be developed into a new technique to control the texture of carbon, which may be important in the production of various carbons from filler cokes and binder pitch and also of carbon–carbon composites. In carbon–carbon composites, texture control of the matrix carbon has been pointed out to be very important to give high mechanical strength of the composites [13, 14].

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