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Texture and graphitizability of carbons made from pitch and phenolic resin mixtures

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Benzene-soluble pitch and two types of phenolic resin, resol- and novolac-type, were mixed by using pyridine. After removing pyridine, the mixtures were carbonized at 600° C and then heat-treated at 3000° C. By solvent-mixing, homogeneous optical textures within the carbons were found to be obtained, though mechanical-mixing led to heterogeneity. Changes in optical texture from coarse mosaic to isotropic through fine mosaic were observed in the carbons in the range of resin content between 40 and 60% for the pitch–resol-type-resin system, and between 30 and 40% for the pitch–novolac-type-resin system. The transitions from well graphitized to poorly graphitized carbons were observed on the 3000° C-treated samples in the same range of resin content. In the carbon fibre–carbon composites prepared by using these pitch–phenolic-resin mixtures as matrix, fine mosaic texture in the matrix appeared with a lower content of resin.

1. Introduction

It has been pointed out by different authors that the texture of carbon materials governs their high temperature behaviour and principal properties: the microtexture observed under an electron microscope determines graphitization behaviour of carbons [1], formation and growth of meso-phase in pitches determine the properties of resultant cokes [2] and preferred orientation of graphite-like layers along the fibre axis is an important factor for improving the modulus of carbon fibres [3].

In composite materials, carbon fibre–carbon and ceramic–carbon, the control of texture of the carbon matrix is necessary to obtain high mechanical strength, as well as the selection of suitable fillers. Thermoplastic carbon precursors, mostly pitches, are used as the matrix for carbon fibre–carbon composites [4, 5], to prevent carbonization shrinkage and the formation of pyrolysis cracks in the matrix derived from the thermosetting phenolic resins. Mackay and Courtney [6] reported that carbon fibre–carbon composites with high mechanical strength were prepared by using mixtures of pitch and phenolic resin as a precursor for the matrix. Carbon matrices with a random arrangement of small oriented domains (fine mosaic texture) are desired. Ishibashi and Sakaguchi [7] suggested that high mechanical strength of the ceramic–carbon composites made from MgO and the pitch–phenolic-resin mixture is attributable to the fine mosaic texture of the carbon matrix. However, homogeneous and fine mosaic texture in the carbon matrix has never been obtained in these works. Recently, Forrest and Marsh [8] obtained carbons with a homogeneous texture from co-carbonization of a coal extract and an industrial resin. In our previous paper [9], solvent-mixing was shown to be effective in order to obtain carbons with a homogeneous texture from mixtures of pitch and phenolic resin which are immiscible by mechanical mixing.

The aims of the present work are to obtain the carbons with homogeneous optical textures from pitch–phenolic-resin systems and also to control the texture of the resultant carbons by changing the mixing ratio. In order to obtain a homogeneous fine mosaic texture in the carbon matrix of composites, preliminary studies were also made.

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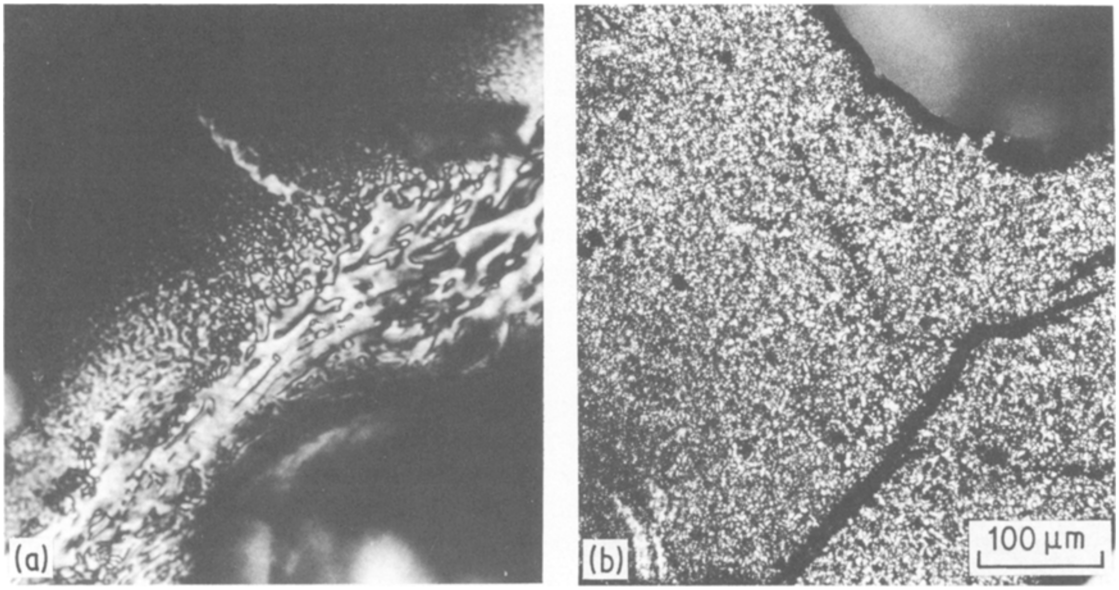

Figure 1 Polarized light micrographs of the carbons from the mixtures of pitch and resol-type resin with mixing ratio of 1 : 1: (a) mixed by using an agate mortar, (b) mixed by using pyridine.

2. Experimental

For the pitch component, a benzene-soluble fraction was obtained from a coal tar pitch by the freeze-drying method. Two different types of phenolic resin†, resol- and novolac-type, were used, both of which were soluble in pyridine. The former contains about 30% of ethylene glycol. The two components, pitch and resin, were mixed in pyridine to give selected ratios of the phenolic resin to pitch. The pitch–phenolic-resin mixtures were obtained by removing pyridine *in vacuo* at about 60° C. The mixtures of 5 g thus prepared were cured at 120° C for 5 h in air and then post-cured at 200° C for 5 h in a flow of nitrogen gas. The samples were then carbonized at 600° C for 3 h in a flow of nitrogen. The heating rate was 1° C min^{-1}. A vertical furnace and pyrex glass tube with 18 mm inner diameter and 150 mm height were used.

The carbon yield from the mixtures was determined from the change in weight between post-cured and carbonized samples. Optical textures of resultant carbons were examined in polished sections under a polarized light microscope. The carbonized samples were heat-treated at 3000° C for 30 min in nitrogen gas. X-ray diffraction profiles of 002 and 110 lines were measured by using Ni-filtered and Cu*Kα* radiation, and the average interlayer spacing $\bar{d}_{002}$, crystallite thickness $L_c(002)$ and crystallite diameter L_a were determined by referring to the inner standard of silicon. Optical textures of the 3000° C-treated samples were also observed.

The carbon fibre–carbon composites were prepared by using these pitch–phenolic-resin mixtures as a matrix carbon precursor. A bundle of PAN-based carbon fibres aligned unidirectionally was soaked in the pyridine solution of the mixtures with various phenolic resin contents, the mixture penetrating into the voids between the fibres, at reduced pressure. After vaporizing the solvent pyridine in vacuo at 70° C, the sample was cured at 120° C and post-cured at 200° C. This penetration was repeated four times. The carbon fibre–carbon composites 40 x 8 x 2 mm in size were obtained by carbonization under the same condition as described before.

As a comparison, the mechanically made mixture of benzene-soluble pitch and resol-type phenolic resin was also carbonized after curing and post-curing.

3. Results and discussion

3.1. Importance of solvent mixing

Optical micrographs in Fig. 1 show a remarkable effect of solvent-mixing on the texture of resultant

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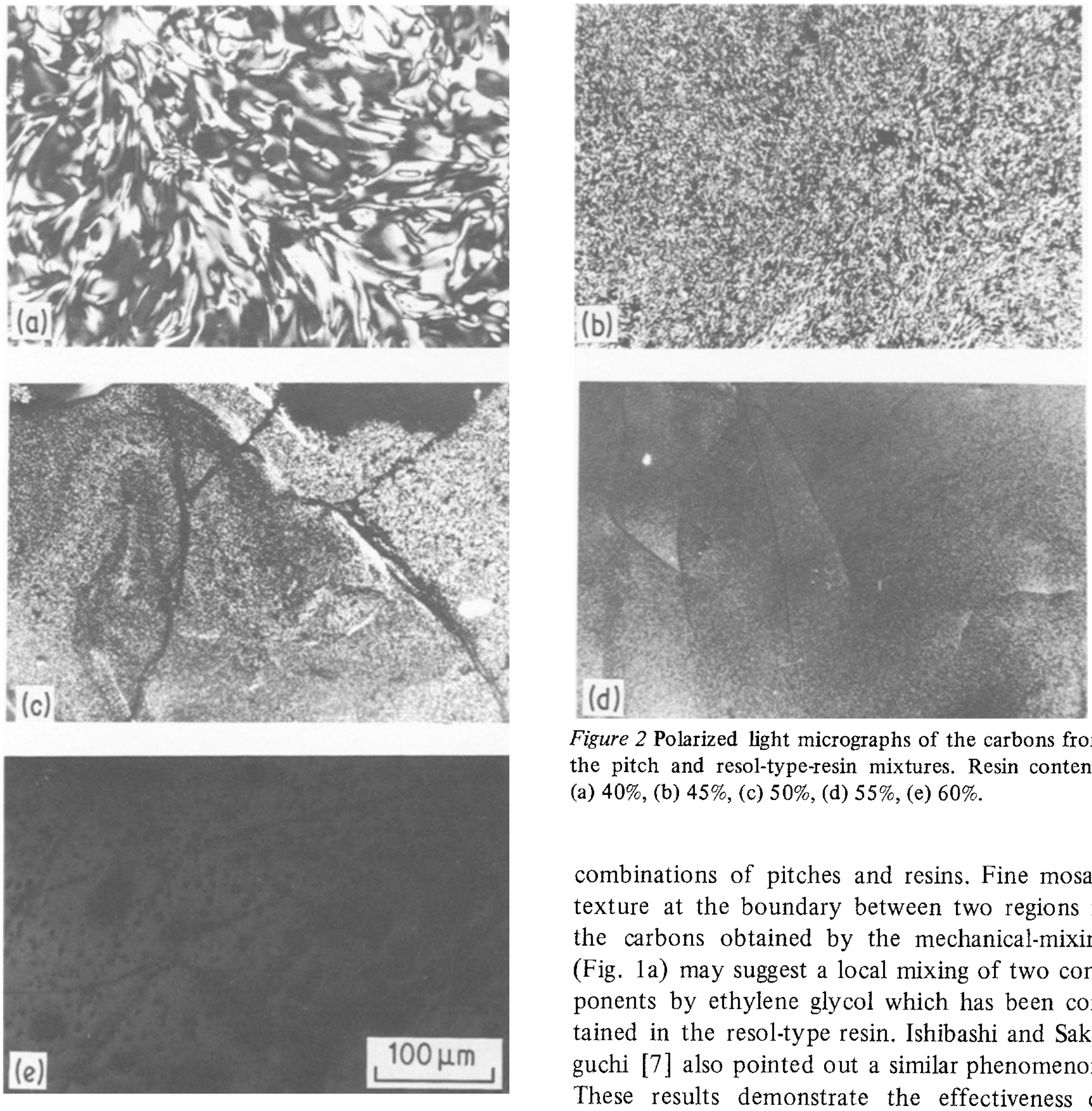
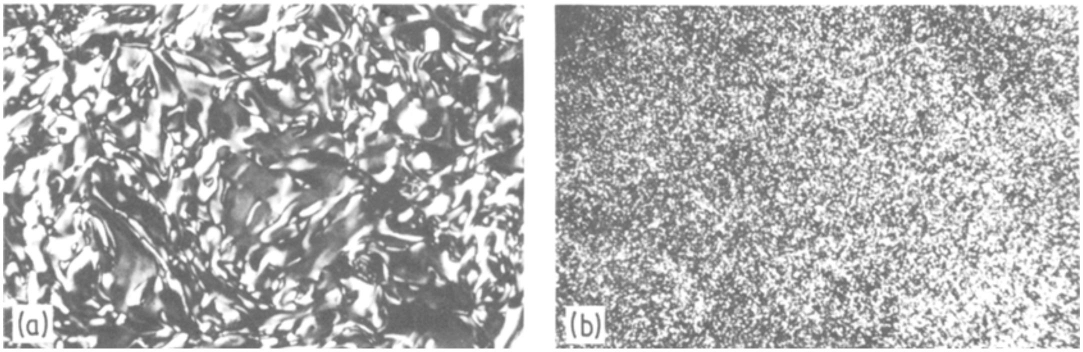


Figure 2 Polarized light micrographs of the carbons from the pitch and resol-type-resin mixtures. Resin content: (a) 40%, (b) 45%, (c) 50%, (d) 55%, (e) 60%.

carbons: mechanical-mixing leads to a heterogeneous texture of anisotropic coarse mosaics and isotropic regions, which indicates the independent carbonization of each component, pitch and resin. Solvent-mixing, on the other hand, leads to a fine mosaic texture which extends homogeneously within the particles of the sample. Forrest and Marsh [8] found a combination of a coal extract and an industrial resin to result in carbons with homogeneous texture by mechanical-mixing. Although the details on the samples were not described, the starting coal extract might contain a large amount of a low molecular weight component which can dissolve the resin. They also obtained carbons with heterogeneous texture from other combinations of pitches and resins. Fine mosaic texture at the boundary between two regions in the carbons obtained by the mechanical-mixing (Fig. 1a) may suggest a local mixing of two components by ethylene glycol which has been contained in the resol-type resin. Ishibashi and Sakaguchi [7] also pointed out a similar phenomenon. These results demonstrate the effectiveness of solvent-mixing for texture control of resultant carbons and justify the use of the solvent-mixing technique of the present study.

3.2. Changes in optical texture and carbon yield with resin content

Changes in optical texture of the carbons with different contents of the resol-type resin are shown in Fig. 2. Using mean spacings between extinction contours as a measure of mosaic unit, this decreases gradually with increase in resin content. Between 40 and 60% of resin content, fine mosaic texture is observed. Above a resin content of 60%, the optical texture is isotropic, that is, the size of the mosaic unit is too small to be detected under the optical microscope, as with



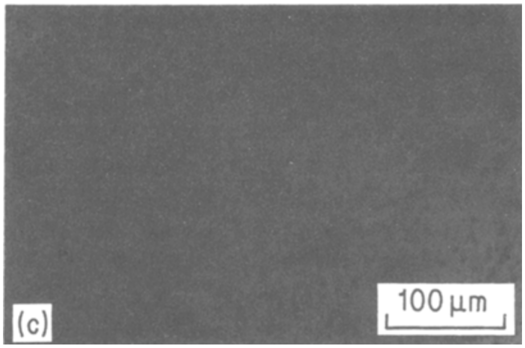


Figure 3 Polarized light micrographs of the carbons from the pitch and novolac-type-resin mixtures. Resin content: (a) 30%, (b) 35%, (c) 40%.

the carbon from phenolic resin. Below 40% of resin content, coarse mosaic texture was observed, as with the carbon from pure pitch (benzene-soluble fraction).

For the mixture of pitch and novolac-type resin, the same transition in optical texture was found between resin contents of 30 and 40%, as shown in Fig. 3. The transition occurs at a lower and in a narrower range of resin content in comparison with the pitch–resol-type-resin system. In this transitional range, the size of the mosaic unit decreases gradually with increasing resin content.

Optical texture, in other words, the size of the mosaic unit in bulk mesophase, was pointed out to be mainly determined by the fluidity of a phase which had been passed through during carbonization of a precursor, though there was no quantitative relation between viscosity and texture of the resultant carbons. The pitch gives a liquid phase before its carbonization and leads to coarse mosaic texture. Therefore, the homogeneous mixtures between these two precursors are expected to give an intermediate phase during the carbonization process, of which the fluidity changes gradually with mixing ratio. This seems to be the case in the pitch–phenolic-resin systems mixed by using a solvent.

As noted before, the resol-type phenolic resin contained about 30% of ethylene glycol and the resin content in the mixtures was calculated by including it. After post-curing of the mixtures, however, most of ethylene glycol was driven out. Therefore, the resol-type resin carbonized at 600° C with the pitch is 70% of the nominal content of resin. The range of resin content at which a fine mosaic texture was found for the pitch–resol-type-resin system corresponds to the range of real resin content of 28 to 42%. This is exactly the same range as found for the pitch–novolac-type-resin system.

Fig. 4 shows the change in carbon yield at 600° C with resin content in the starting mixtures. The carbon yield slightly increases with increase in resin content, from 56% for the pitch to 62% for the resins. Any indication of an anomalous increase

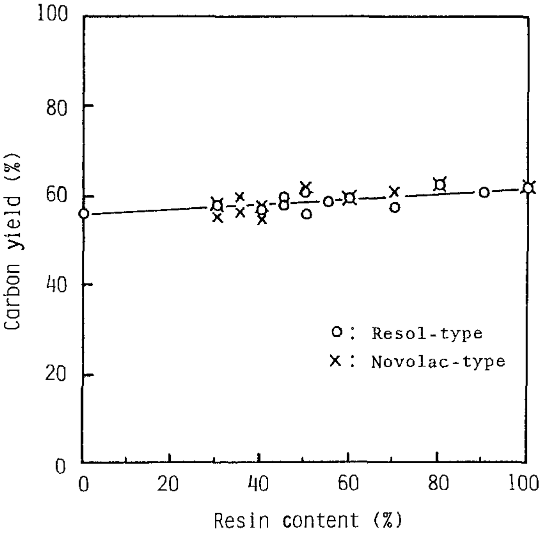


Figure 4 Changes in carbon yield at 600° C from the pitch–phenolic-resin mixtures with resin content.

in carbon yield was not observed in either system. Between resol-type and novolac-type resins, no difference in carbon yield is observed, probably because the carbon yield was calculated on the basis of the weight loss after the post-curing at 200° C, i.e. almost all ethylene glycol contained in the resol-type resin was excluded in the calculation of carbon yield.

3.3. Graphitiziability of resultant carbons

The optical texture was found to govern the graphitizability of the carbons obtained, as pointed out by various authors. The transition from well graphitized to poorly graphitized carbons after the heat-treatment at 3000° C was observed at the same range of resin content as that in optical texture was found. In Fig. 5, 002 diffraction profiles are shown for the 3000° C-treated carbons. With decreasing resin content in the starting mixtures, the 002 diffraction profile sharpens and shifts to higher angles. This change in diffraction profile corresponds to that in optical texture shown in Fig. 2, the isotropic texture corresponding to a broad profile at low angles of diffraction and the coarse mosaic texture to a sharp profile at high angles.

For the pitch–novolac-type-resin system, the same change in 002 diffraction profile for the 3000° C-treated carbons was observed, corresponding also to the changes in optical texture of Fig. 3.

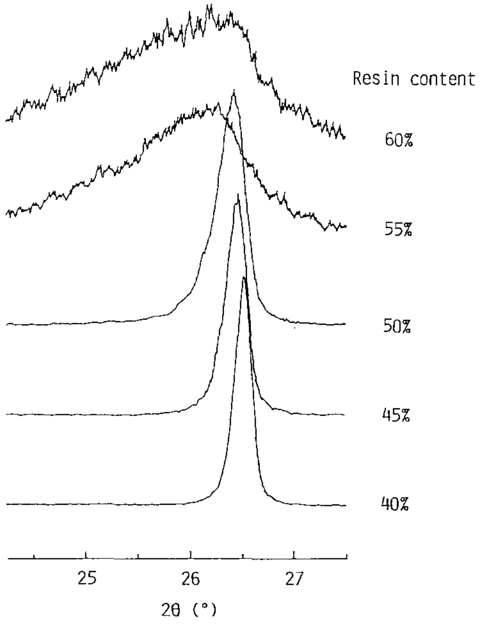


Figure 5 X-ray diffraction profiles of 002 line of the 3000° C-treated carbons from pitch and resol-type-resin mixtures.

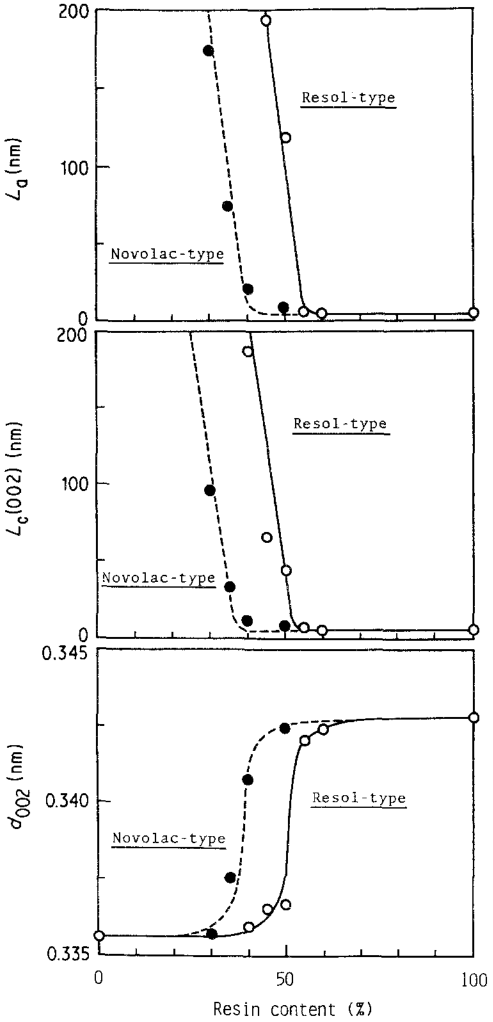


Figure 6 Changes in X-ray structure parameters of the 3000° C-treated carbons with resin content in starting mixtures: (a) pitch–resol-type-resin system, (b) pitch–novolac-type-resin system.

In Fig. 6, X-ray structure parameters, $\bar{d}_{002}$, $L_c(002)$ and L_a, are plotted against resin content in the starting mixtures. Sharp changes in the structure of the 3000° C-treated carbons are clearly seen at 55% for the pitch–resol-type-resin system and at 40% for the pitch–novolac-type-resin system: sharp increases occur in $\bar{d}_{002}$ and decreases in $L_c(002)$ and L_a, namely, from well graphitized to poorly graphitized. A rather steep increase in interlayer spacing $\bar{d}_{002}$ is observed at the resin content which leads to a very fine mosaic unit, in other words, just before changing to isotropic texture. Similar results were reported by Oya *et al.* [10].

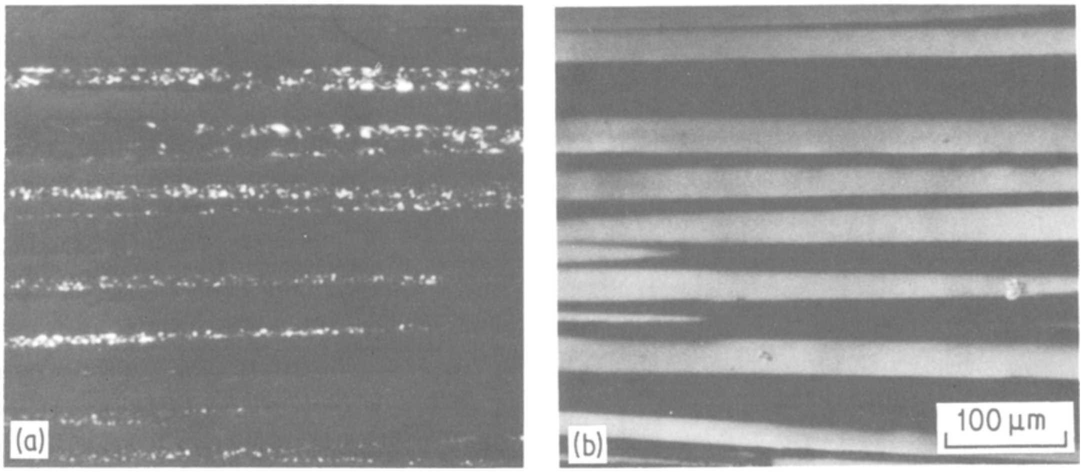


Figure 7 Polarized light micrographs of carbon fibre–carbon composites made by using the pitch and resol-type-resin mixtures as the matrix precursor. Resin content: (a) 30% and (b) 45%.

3.4. Preparation of carbon fibre–carbon composites

When these mixtures were used as a matrix for carbon fibre–carbon composites, a fine mosaic texture was found to occur at a much lower content of resin. In Fig. 7, the polarized light micrographs of the composites prepared are shown. After the carbonization at 600° C, the matrix carbon formed from a mixture with 30% resol-type phenolic resin shows a fine mosaic texture, but the mixture with 45% resin leads to the matrix carbon of isotropic texture; the former mixture itself gives coarse mosaic and the latter fine mosaic texture.

This is probably due to the hindrance of the matrix precursor by the presence of carbon fibres. This fact suggests the importance of fluidity of the intermediate liquid phase from the precursor to the carbon for determining the texture of resultant carbons.

4. Conclusion

Pitch and phenolic resins are known to be two extremes in carbonization and graphitization behaviours; the former carbonizes through fluid phase and gives good orientation of carbon layers, usually resulting in graphitizing carbons, but the latter carbonizes through solid phase and gives random orientation of layers, usually in non-graphitizing carbons. The mechanical-mixing of these two carbon precursors and subsequent carbonization were found to lead usually to carbons with the texture of complex heterogeneity, mainly because of the lack of mutual solubilities during mixing of precursors and also carbonization. However, mixing by using a solvent which could dissolve both precursors was found to lead to carbons with homogeneous texture. The optical texture of resultant carbons was also found to be able to be controlled from a large unit of mosaic to units too small to be detected under an optical microscope (isotropic in appearance) by changing their mixing ratios.

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