



## Graphitization of Mixture Precursor with Pitch and Resin by Thermal-Mechanical Blending†

KWANG-YOUN CHO\* and KHOS ERDENE

Department of Nano-Convergence Intelligence Materials, Korea Institute of Ceramics Engineering and Technology, Seoul, Republic of Korea

\*Corresponding author: Fax: +82 2 32827711; E-mail: kycho@kicet.re.kr

AJC-17455

Successful blending of pitch and phenol resin is introduced by applying thermal-mechanical stirring during melting of pitch and resin. The method of mixing of pitch and resin on impregnation into carbon fiber carbon matrix has not been reported so far. After graphitization at 2500 °C in inert atmosphere, as a promising result, graphite with over 72 % graphitization could be obtained on resin content 70 % above and the oxidation starting temperature was remarkably decreased. This it thought to promote an effective thermal-mechanical blending of pitch and resin, which are normally difficult to mix, while raising the oxidation temperature (*i.e.*, slowing the oxidation rate) by changing the graphite crystallinity. The origin of the improvement is discussed on the basis of several analytical results including FE-SEM, TG and XRD.

**Keywords:** Pitch, Resin, Graphite, Blending, Crystallinity, Nanocomposite.

### INTRODUCTION

Carbon fiber reinforced carbon (C/C) composite can be applied in various fields due to their excellent properties like low density, high strength, high thermal conductivity and low thermal expansion coefficient. In order to fabricate carbon fiber reinforced carbon composite, many material including pitch, phenol, epoxy *etc.* can be used as precursor of carbon matrix<sup>1,2</sup>. Carbon matrix derived from each precursor shows the difference in the thermal and mechanical properties. Among these precursors, a pitch is usually used for their low price, high carbon yield and easy handling during the process. Also carbon matrix from pitch has the high graphite crystallinity and high thermal conductivity. But the ablation property of carbon matrix from pitch was bad because of the high graphite crystallinity and high thermal conductivity<sup>1,2</sup>. In order to overcome this situation, pitch precursor is exchanged by phenol resin. The ablation property was enhanced by exchanging the carbon precursor from pitch to phenol resin. Many researchers reported that graphite crystallinity and thermal conductivity of the carbon matrix derived from phenol resin was lower than graphite crystallinity and thermal conductivity of the carbon matrix derived from pitch<sup>3-5</sup>. But the handling phenol resin during process is difficult for their viscosity. So many researchers investigated how to mix the pitch and phenol. Usually pitch and phenol resin mixture was fabricated by mixing pitch

and phenol in the solvent<sup>6,7</sup>. So, in this process, the mixture had to be evaporated. Also to fabricate the carbon fiber reinforced carbon composite, more process cycles required because the mixture solvent has the low carbon yield.

In this study, we intended to overcome this by thermal-mechanical mixing of pitch and phenol resin. To fabricate uniform mixture of pitch and phenol resin, both precursors were melted and stirred at their melting temperature. To confirm the micro structure and nanocomposite of the fabricated carbon matrix, optical microscopy analysis was used. Also, XRD and FT-IR analysis was performed in order to confirm the graphite crystallinity of synthesized carbon matrix.

### EXPERIMENTAL

Carbon matrix precursors used in this study were pitch and phenol resin. Pitch was coal-tar pitch purchased from OCI Company Ltd. (Korea). And phenol resin was novolac and purchased from Shinheung chemical Ltd. (Korea). Pitch and phenol resin were mixed with the weight ratio 7:3, 5:5 and 3:7. Then pitch and phenol resin mixture put in beaker on hot-plate were heated to 250 °C with flowing Ar gas to prevent the oxidation curing and when the mixture was melted like liquid. The mixture was stirred on hot plate at 100 rpm for 0.5 h. After stirring, the mixture was cooled to room temperature. The mixture precursor was analyzed to confirm the micro-

†Presented at The 8th ICMMA-2014, held on 27-29 November 2014, Hoseo University, Chungnam, Republic of Korea

structure by the optical microscopy. For graphitization, the mixture put in graphite crucible was heated up to 2500 °C under 50 bar nitrogen gas pressure with HIP. The graphite derived from mixture was analyzed to confirm crystallinity, microstructure and thermal behaviour by the XRD, SEM, Raman, TG. The degree of graphitization was calculated with the following equation:

$$\text{Graphite crystallinity} = [3.44 - d(002)] / [3.44 - 3.354]$$

\*here,  $d(002) = \lambda / 2\sin\theta$  (Brag's law).

## RESULTS AND DISCUSSION

To confirm the carbon yield of the mixture, TGA analysis was performed. Fig. 1 shows the graph of thermogravimetric on pitch, mixture of pitch and phenol resin and phenol resin as a function of temperature. The carbon yield of pitch, pitch and phenol mixture (5:5) and phenol resin was about 43.6, 38.8 and 30.5 wt % respectively. The carbon yield of the phenol resin is smaller than pitch. As the pitch ratio decreased, the carbon yield of the mixture decreased from 43.6 to 30.5 % respectively. There was no effect on increasing of carbon yield by chemical reaction during thermal-mechanical blending pitch and phenol resin. By this result, there was no reaction between pitch and phenol resin. Because pitch and phenol resin have hydrophilic and hydrophobic property respectively.

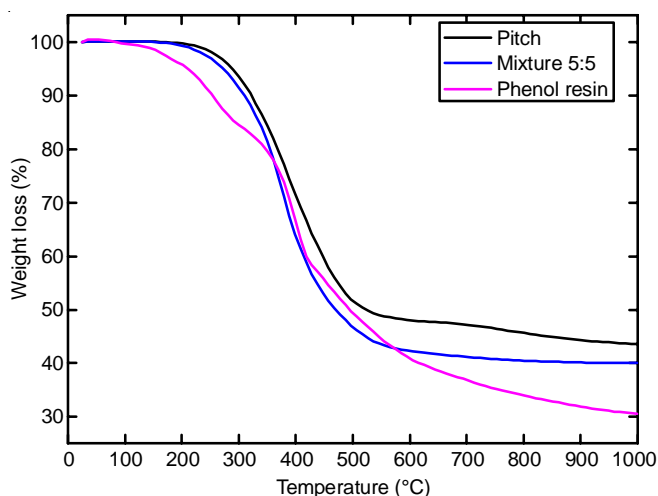


Fig. 1. Thermogravimetric on different mixture ratio as a function of temperature

The microstructure of the mixture was confirmed by the polarizing microscopy analysis. Pitch(a) in Fig. 2 was observed to have one phase. But mixtures were observed to show two phases. In Fig. 2(b), the bright portion was pitch and the dark portion was phenol resin. At the weight ratio of 7:3, it looked that the phenol resin was isolated forming sphere among pitch matrix. And when mixture ratio go to 3:7, the sphere shape of resin observed more. It is thought that mixture was saperated due to difference of hydrophilic and hydrophobic on pitch and phenol resin during cooling at room temperature.

Fig. 3 shows the XRD pattern of graphitization specimen at 2500 °C according to their mixture ratio. Major peaks, indicative of graphite crystallinity, are seen at 23.5 and 43 °C, indicating the production of crystalline graphite. The graphite

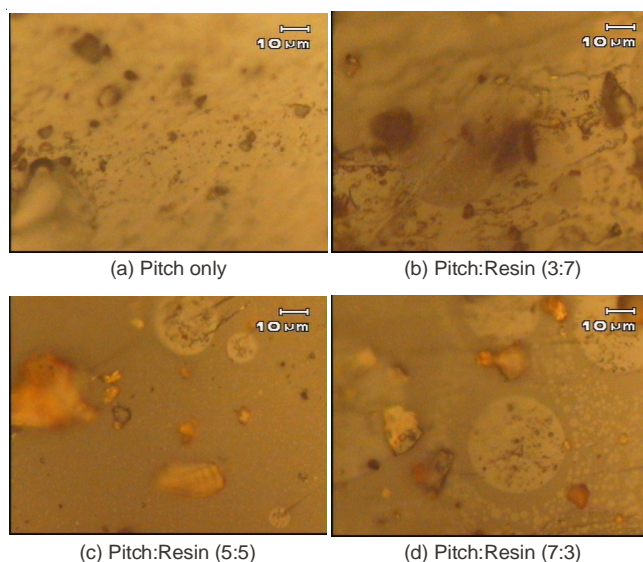


Fig. 2. Polarizing microscopy graphs of mixture as a function of mixture ratio

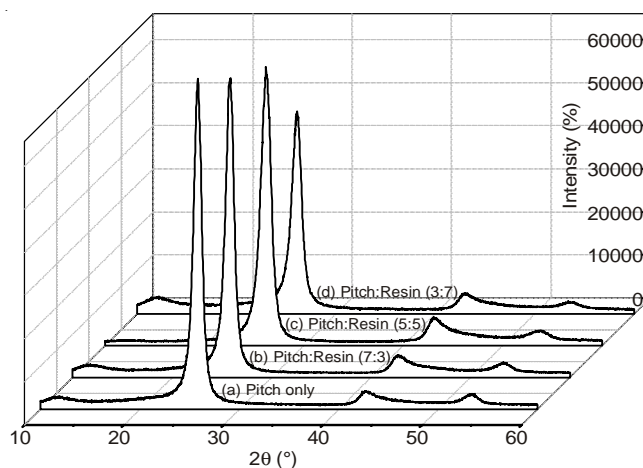


Fig. 3. XRD pattern of graphitization specimen at 2500 °C according to their mixture ratio

specimen (a), which was changed from the pitch, exhibited the strongest and sharpest peak. However, the graphite specimen (d), which was transformed from the mixture with the highest phenol resin content, exhibited the weakest peak and relatively large full-width at half maximum. This suggests that the pitch easily transforms into crystalline graphite, while the phenol resin is not as easily transformed.

Fig. 4 is a graph that shows the degree of graphitization of the specimens after graphitization according to their mixture ratios. The degree of graphitization was the highest, 87 %, in the graphite specimen transformed from the precursor formed only from pitch, whereas the graphite specimen formed from the mixture having high phenol resin content was the lowest at 72 %. Resin is generally known to be a difficult precursor to transform into crystalline graphite even with a thermal treatment over 2500 °C. In other words, crystallization does not happen according to the ribbon structure model of Jenkins-Kawamura *et al.*<sup>8</sup> or the basket model of Shiraishi<sup>9</sup>; instead, it stays in its amorphous state. However, with the blending of the pitch, a relatively high degree of graphitization is obtained.

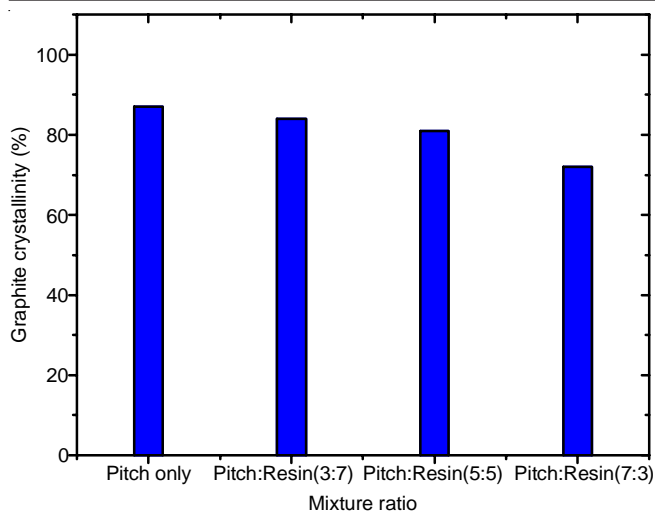
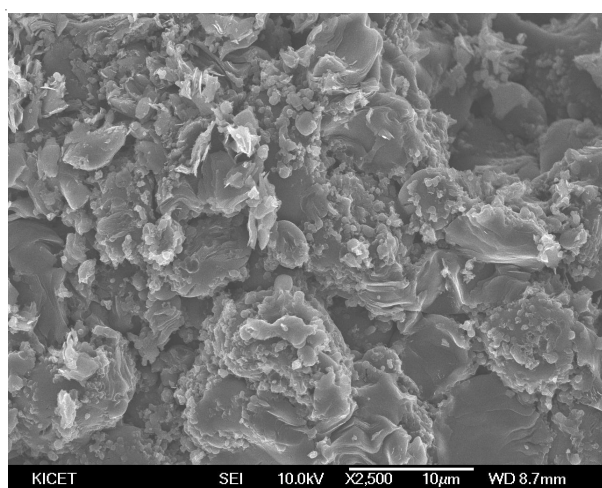
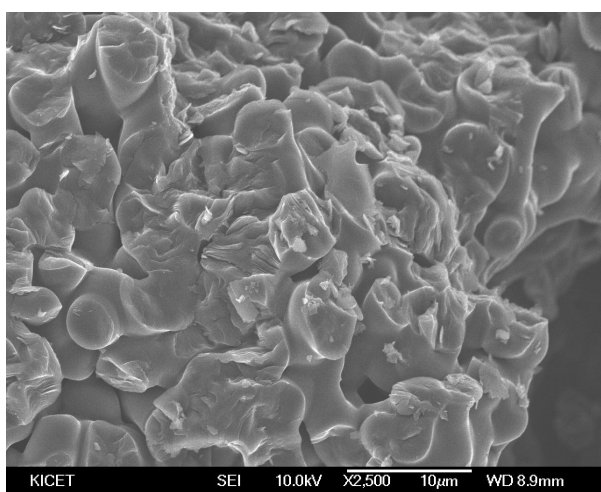


Fig. 4. Graphite crystallinity of the specimens after graphitization according to their mixture ratios

Fig. 5 shows a fractured surface of the graphite specimen transformed from the mixture precursor fabricated with different mixture ratios. In the fractured surface (a) from the precursor composed of pure pitch, the layered structure and the end of the crystalline graphite are clearly observed. On



(a) Pitch only



(b) Pitch:Resin (7:3)

Fig. 5. Fractured surface of the graphite specimen transformed from the mixture precursor fabricated with different mixture ratios

the other hand, although the fractured surface of the graphite specimen transformed from the mixture precursor having the highest phenol resin content has the layered structure, it was relatively clear and the end of the crystalline graphite in the fractured surface showed a rounded formation. As seen in Fig. 4, the graphite specimen transformed from the mixture precursor with the highest phenol resin content showed low graphite crystallinity relatively, indicating an amorphous state such as the ribbon structure model (15) of Jenkins-Kawamura or the basket model of Shiraishi<sup>9</sup>.

Fig. 6 shows the thermal gravimetric analysis of the graphite specimen transformed from the mixture precursors fabricated with different mixture ratios at 1000 °C. The oxidation initiation temperature for the graphite specimen from the precursor composed of pitch was formed at approximately 650 °C. At the same time, it also showed the fastest oxidation rate. On the other hand, the graphite specimen from the mixture precursor having the highest phenol resin content showed an oxidation initiation temperature of about 740 °C and the slowest oxidation rate. This is thought to occur because a decreased crystalline end and layered structure can easily initiate oxidation, whereas the relatively high phenol resin content is in an amorphous state that is not easily oxidized.

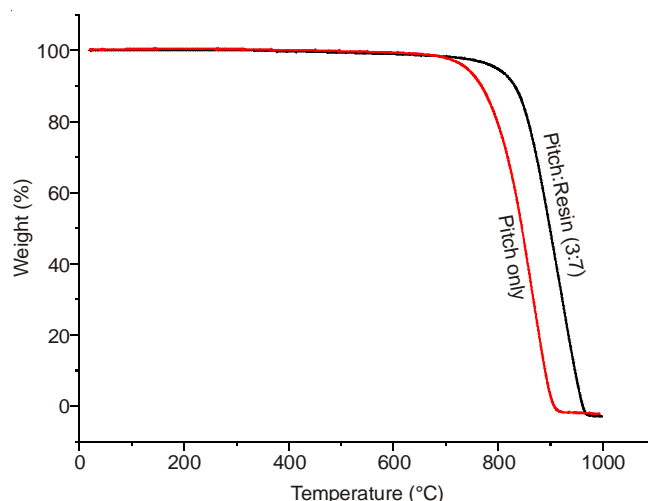


Fig. 6. Thermal gravimetric analysis of the graphite specimen transformed from the mixture precursors fabricated with different mixture ratios

## Conclusions

The following conclusions were obtained about the microstructure and the crystalline state when the mixture precursors, which were thermo-mechanically fabricated by mixing pitch and phenol resin, were graphitized at 2500 °C.

- The graphite specimen transformed from the precursor composed of pitch only showed the highest degree of graphitization, *i.e.*, 87% and that which was transformed from the mixture having the highest phenol resin content showed the lowest, *i.e.*, 72%.

- The fractured surface of graphite specimen transformed from the precursor composed of only pitch clearly showed the layer structure and the end of fractured crystalline graphite. On the other hand, that from the precursor having the highest phenol resin content showed a relatively clear layer structure and rounded edge.

• The graphite specimen transformed from the precursor composed of pitch only exhibited an oxidation initiation temperature of approximately 650 °C and the fastest oxidation rate. However, the graphite specimen transformed from mixture precursor having the highest phenol resin content exhibited an oxidation initiation temperature of 740 °C and the slowest oxidation rate.

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