

# FLEXURAL STRENGTH IMPROVEMENT BY CARBON BLACK ADDITIVES IN PHENOLIC RESIN AS A MATRIX OF CARBON/CARBON COMPOSITES

<sup>1</sup>Tse-Hao Ko, <sup>2</sup>Wen-Shyong Kuo, and <sup>1</sup>Wen-Teng Han

<sup>1</sup>Department of Materials Science  
Feng Chia University, Taichung, Taiwan

<sup>2</sup>Department of Aeronautical Engineering  
Feng Chia University, Taichung, Taiwan

Corresponding author e-mail address: thko@fcu.edu.tw

## Introduction

Carbon/carbon (C/C) composites are primarily developed and designed for high-temperature applications which require strength retention [1-8]. These materials are known for their strength, lightness in weight, and thermal properties. Matrix microstructure plays an important role on mechanical properties of C/C composites. Phenolic resins are used as matrix precursors in C/C properties because they are relatively easy to use to impregnate fibers in traditional polymer composites processing. It can also be expected that the mechanical properties of the final carbonized resins will be dependent on the formation of the microstructures of the resin during pyrolysis.

The present study relates to the effect of carbon black additives on the microstructure of carbon matrix. The thermosetting resin matrix precursor modified by carbon black heat-treated from 230°C to 2500°C was prepared. The microstructure changes, flexural strength, and physical properties were studied.

## Experimental

The resole-type phenol-formaldehyde resin was supplied by Chang Chun Petrochemical Industry, Taiwan, as a 60 wt% solid content solution. The carbon black, N-660 type, was supplied by Korea Steel Chemical Co. Ltd. The samples were systemically prepared by 0, 5, 10, and 15% by weight of carbon black on the basis of the resin. The resin and the carbon black were well blended. The samples were concentrated under vacuum at 70°C for 8 h and then at 80°C for 8 h. The samples were then poured into aluminum plates, and cured in an oven from 80 to 150°C for several hours. Following this, the resin was cured at 160°C for 2 h, and slowly cooled (2°C/min) to room temperature. The cured resins were cut to an appropriate size (6x1x0.3 cm). The cured samples were post-cured in air at 230°C for 32 h. All samples were pyrolyzed at a heating rate of 1°C/min from 25 to 1000°C in nitrogen, respectively. The graphitized resins were graphitized to 1800 and 2500°C at a rate 15

°C/min in an argon flow, respectively.

The flexural strength of the composites was determined using the three-point bending method prescribed by ASTM D790. Fractured composites were examined under a scanning electron microscope (SEM).

## Results and Discussion

The TGA curves for the carbon black, the resin and the resins added with carbon black are shown in Figure 1. When the samples were heat-treated at 1000°C, the total weight loss was 31.6wt% for the carbon black. The values were 55.0wt% for sample R0 (the original resin), 51.6wt% for sample R5 (added with 5wt% carbon black), 46.3wt% for sample R10 (added with 10wt% carbon black), and 35.4wt% for sample R15 (added with 15wt% carbon black). In view of this, it is revealed that carbon black additives can limit the decomposition reaction and the thermal fragmentation, which minimize the weight loss of the resins and increase their carbon yield during the heat-treatment process.

Figure 2 presents the variation in weight loss of all samples after the heat-treatment. The weight loss is determined from the change in weight between cured and heat-treated samples. The weight loss was significant below 800°C, and it was nearly completed by 1800°C. This was due to the condensation of aromatic ribbon molecules in the resin and the volatilization of low molecular weight species. These reactions also led to the shrinkage of the resins during pyrolysis (Fig. 3).

Compared with the behavior of the weight loss, the linear shrinkage occurred continuously above 1000°C (Fig. 3). Above 800°C, the shrinkage was owing to the rearrangement of the carbon structure. Above 1000°C, the shrinkage was very slow. This was attributed to the repacking and crosslink of the glassy carbon structure. At 2500°C, linear shrinkage was 17.4% for sample R0, 16.3% for sample R5, 15.7% for sample R10, and 14.2% for sample R15. The weight loss and the shrinkage of sample R15 was found to improve by about 20% and 18%, over that of R0.

Figure 4 shows the variation in real density of the resins during pyrolysis. Heat-treating temperature affects the real density of samples. When the heat-treating temperature ranged from 800°C to 1800°C, the real density decreases with increasing temperature. This was due to the microstructure rearrangement and the formation of closed pores from open pores. At this stage, the effect of the formation of closed pores was higher than the chemical densification. Therefore, this led to the decrease in the real density of all samples. Above 1800°C, the density increased again, due to the chemical structure change, the condensation, and the cross-linking of the carbon basal phase in the resin. At heat-treatment temperature of 2500°C, the real density of samples R0, R5, R10, and R15 was 1.47, 1.55, 1.59, and 1.60 g/cm<sup>3</sup>, respectively.

Figure 5 shows the effect of carbon black addition on the flexural strength of the resins during pyrolysis. It is found that addition of carbon black increased the flexural strength of the resins during pyrolysis. At 2500°C, the flexural strength of samples R0, R5, R10, and R15 was 14.5, 46.8, 52.3, and 51.0 MPa, respectively. The addition of carbon black was effective to promote the flexural strength of the resin during heat-treatment. The flexural strength increased over 300% with only 5wt% addition.

### **Conclusion**

The above concluded that the resin additive with carbon black process would promote the condensation reaction and the gas evolution in pyrolysis. This process not only decreased the weight loss but also limited the shrinkage of the resins with carbon black. The weight loss during pyrolysis can be improved by 20%.

The heat-treated resins with carbon black had a greater flexural strength by over 300%, developing from the original resin. At 2500°C, the flexural strength of the original resin was 14.5MPa, that of the resins with carbon black being 46.8, 52.3, and 51.0 MPa for samples R5, R10, and R15, respectively.

### **Acknowledgements**

The authors would like to thank the National Science Council for its financial support of this project (No#: NSC91-2216-E-035-007).

### **References**

- [1] Fitzer E. The future of carbon-carbon composites. *Carbon* 1987;25(2):163-90.
- [2] Buckley JD. Carbon-carbon, an overview. *Ceramic Bulletin* 1988;67(2):364-8.
- [3] Weissshaus H, Kening S, Siegmann A. Effect of materials and processing on the mechanical properties of C/C composites. *Carbon* 1991;29(8):1203-20.
- [4] Jain PK, Bahl OP, Manocha LM. Effect of carbon fiber type on the mechanical performance of carbon/carbon composites. *SAMPE Quarterly*, 1992, April, 43.
- [5] Manocha LM, Yasuda E, Tanabe Y, Kimura S. Effect of carbon fiber surface treatment on mechanical properties of C/C composites. *Carbon* 1988;26(3):333-8.
- [6] Manocha LM, Bahl OP. Influence of carbon fiber type and weave pattern on the development of 2D carbon-carbon composites. *Carbon* 1988;26(1):13-22.
- [7] Ko TH. The effect of pyrolysis on the mechanical properties and microstructure of carbon fiber-reinforced and stabilized fiber-reinforced phenolic resins for carbon/carbon composites. *Polymer Composites* 1993;14(3):247-56.
- [8] Fitzer E, Geigl KH, Huttner W. The influence of carbon fibre surface treatment on the mechanical properties of carbon/carbon composites. *Carbon* 1980;18(4); 265-71.

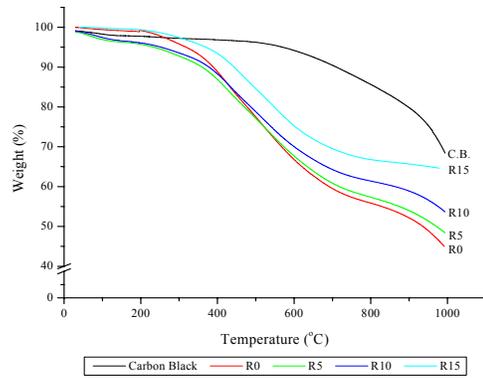


Fig. 1 TGA curves of carbon black, resin, and resins added with carbon black.

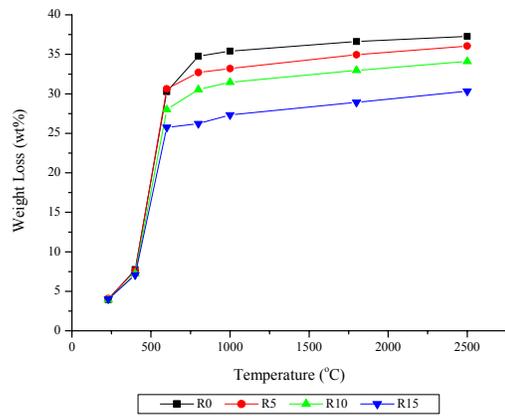


Fig. 2 Variation of weight loss of resin and resins with carbon black during pyrolysis.

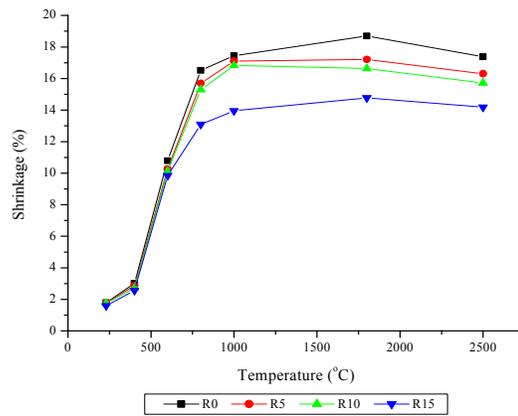


Fig. 3 Variation of shrinkage of resin and resins with carbon black during pyrolysis.

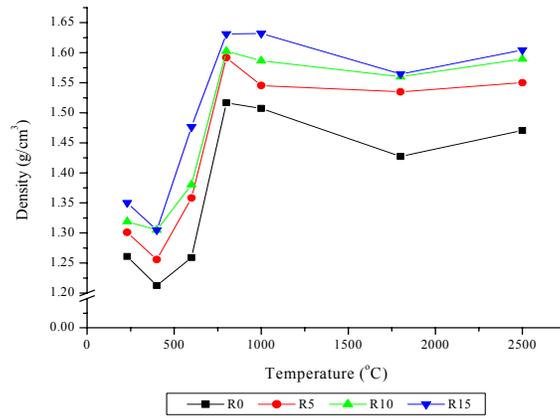


Fig. 4 Variation of real density of resin and resins with carbon black during pyrolysis.

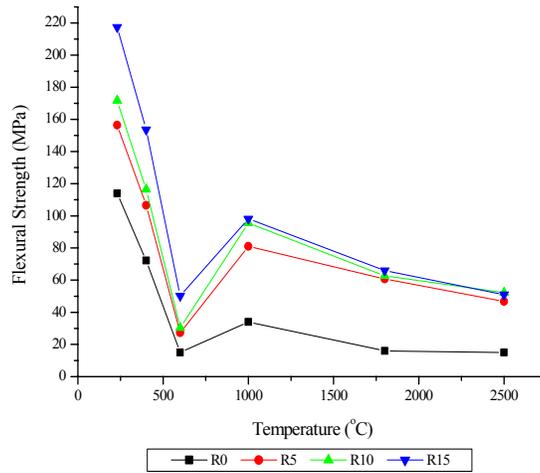


Fig. 5 Variation of flexural strength of resin and resins with carbon black during pyrolysis