Available online at www.sciencedirect.com

SCIENCE DIRECT®

Materials Letters 59 (2005) 2746 – 2750

materials letters

www.elsevier.com/locate/matlet

Influence of adding MCMBs into carbon/carbon composites reinforced by PAN Base No-woven carbon fabrics on their microstructure and performances

Hsien-Lin Hu[a,*], Tse-Hao Ko[a], Wen-Shyong Kuo[b], Yan-Ju Su[a]

[a]*Department of Materials Science and Engineering, Feng Chia University, Taichung, Taiwan, ROC*
[b]*Department of Aeronautical Engineering, Feng Chia University, Taichung, Taiwan, ROC*

Received 3 November 2004; accepted 22 April 2005
Available online 31 May 2005

Abstract

Carbon/carbon composites were prepared from PAN Base No-woven carbon fabrics, resol-type phenolic resin and Mesocarbon Microbeads (MCMBs), which is derived from coal tar. In this study, the effect on microstructure, flexural strength, electric conductivity and thermal conductivity of carbon/carbon composites with MCMBs contents ranging from 0 to 30 wt.% were examined during pyrolysis. The results showed that the carbon/carbon composite with addition of 10~30 wt.% MCMBs has a higher density and preferred orientation than those of carbon/carbon composite without MCMBs during heat treatment. These composites also exhibited an improvement in flexural strength from 21.4% to 34.0%. These composites also showed an improvement in electric conductivity from 25.0% to 59.6% and that in thermal conductivity from 10.5% to 18.0%.

Keywords: Aerospace materials; Composites materials; Polymer; X-ray technique; Thermal properties; Microstructure; Electrical properties

1. Introduction

Carbon fiber reinforced composites (C/C) are potentially useful materials in applications requiring strength and toughness even at high temperature, combined with low weight [1–3]. Due to these excellent properties, the interest of aerospace industry in carbon/carbon composites has rapidly increased over the past decades [4,5]. In earlier research, expensive high-modulus carbon fibers and techniques have been used to produce these composites. However, the high demand for industrial applications has resulted in the development of alternative fabrication routes with lower costs, and controlled mechanical and thermal properties. In aerospace applications, 2D-C/C composites have been made from woven carbon fabrics as reinforcements.

The physical and chemical characteristics of composites depend strongly on the precursors of the matrix used and the method of fabrication. Phenolic resin is extensively employed as matrix precursors in forming C/C composites because they are relatively to impregnate with fibers and therefore yield a large amount of carbon 40–50% [6]. However, the carbon derived from phenolic resin is an amorphous carbon (non-graphitizable carbon).

Several groups are studying of using MCMBs as a precursor to the matrix [7,8] because MCMB after pyrolysis is graphitizable carbon and shows great crystalline. Unfortunately, MCMB as a matrix precursor for carbon/carbon composites shows a bad ability to impregnate reinforcements. Therefore, we try to mix MCMBs and phenolic resin together to improve crystalline of composites and the ability to impregnate reinforcements; expecting that it can improve performances on thermal conductivity and

---

* Corresponding author. Tel.: +886 4 24517250x5303; fax: +886 4 24518201.
E-mail address: watterhu@pchome.com.tw (H.-L. Hu).

0167-577X/$ - see front matter © 2005 Published by Elsevier B.V.
doi:10.1016/j.matlet.2005.04.050

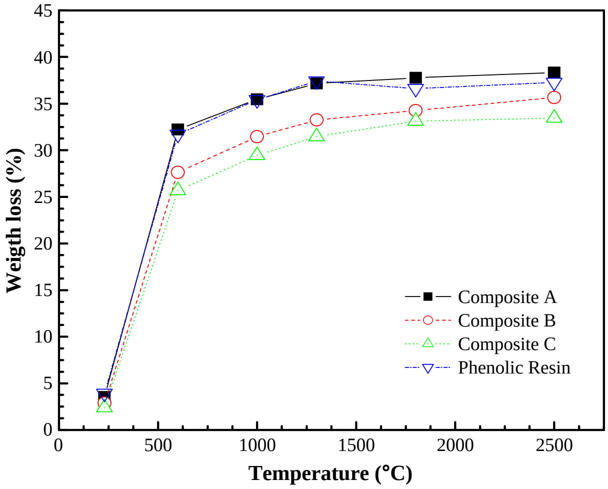

Fig. 1. Weight loss variation of composites A, B and C at various temperatures.

electrical conductivity, which strongly relies on crystalline of carbon.

2. Experiment

PAN Base No-woven carbon fabrics have been carbonized at 1000 °C (Toho Rayon. Co. Ltd. Japan). Resol-type-phenol-formaldehyde resin (Chang Chum Petrochemical Industry Co. Taiwan) was used as a matrix precursor. The MCMBs (China Steel Chemical Co. Taiwan) were extracted from coal tar. Zero weight percent, 10 and 30 wt. % MCMBs were in respect to phenolic resin and then added to resin and mixed with phenolic resin as matrix precursors of C/C composite. PAN Base No-woven carbon fabrics were embedded into pure resins, resin added with 10 wt.% MCMBs and resin added with 30 wt.% MCMBs for 30 min in a vacuum, respectively. Secondly, the impregnated samples were cured at 80 °C for 2 h and hot-pressed at 30 kg/cm^2 and 120 °C for 30 min, and at 160 °C for 10 min. Then, the polymer composites were cut to an appropriate size. Finally, the cut samples were stabilized at 230 °C and pyrolized at a heating rate of 0.5 °C/min up to 600, 1000 and 1300 °C for carbonization; then, these composites were heat treated at a heating rate of 10 °C/min up to 1800 and 2500 °C for graphitization.

The C/C composites were studied by using an Olympus BHT apparatus on the polished surfaces. The texture of the aromatic layers with respect to the fiber and MCMB was determined by a crossed polarizer with a λ retarder plate. The real density was measured using an AccuPyc 1330 Pycnometer. The thermal conductivity of the C/C composites was determined using a Micro300 (Holometrix, USA) according to ASTM 1461 C 714. The electrical resistivity and conductivity of composites were measured using Mitsubishi Chemical MCP-T600 and the four point probes method.

An X-ray diffractometer with Cu K_α radiation sources was utilized to study the microstructures of the composites. The Raman spectrometer used here was a Renishaw instrument with a Raman imaging microscope system 2000, using the 514.5 nm line of an argon ion laser as the incident radiation.

3. Results and discussions

3.1. Variation in weight loss during pyrolysis

The A, B and C composites were derived from pure resin, from composite derived from resin mixing 10 wt% MCMBs and from composite derived from resin mixing 30 wt.% respectively. For all composites, the weight loss could be regarded as resulting in the volatilization of species of low molecular weight from phenolic resin and MCMBs below 1000 °C since reinforcements have been carbonized at 1000 °C. Obviously, the weight losses of the composites to which MCMBs have been added are less than those of composites without MCMBs in Fig. 1. MCMB is a mild product of the carbonization of pitch; it appears as the temperature rises from 400 to 600 °C [9,10]. Numerous small molecules became resealed during the fabrications of MCMBs. Therefore, the weight loss of MCMB after carbonization is smaller than phenolic resin. This factor is considered for the reduced weight loss of composites to which MCMB is added. At the pyrolysis temperature from 230 to 600 °C, the weight loss in various composites increased dramatically due to the volatilization of small molecules from phenolic resin such as H_2O, HCN, NH_3, N_2, CO_2, CO and other gases [11–13]. The weight loss of all composites at the temperature from 600 to 1000 °C tends to change only moderately since almost H_2O molecules were released at this temperature range. Above 1300 °C, the small molecules were almost volatized from the resin and carbon atoms and began arranging in matrix. Following graphitization of the composites A, B and C at 2500 °C, their weight losses were 38.3, 35.7 and 33.45 wt.%, respectively.

3.2. Density

The variations in density of carbon/carbon composites at various heat treatment temperatures are shown in Fig. 2. There are two factors affecting carbonization of composites. One is chemical

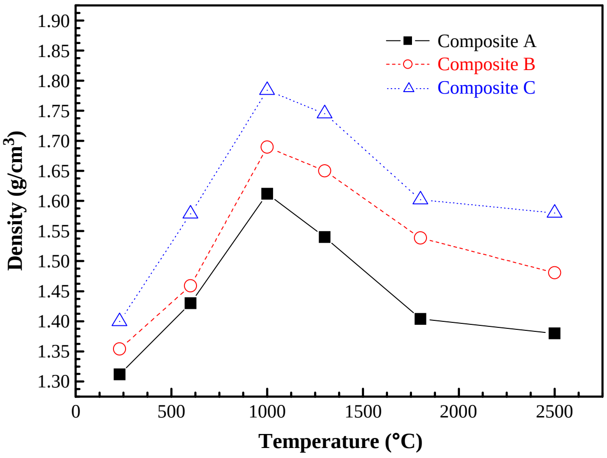

Fig. 2. Experimental density variations for composites A, B and C during carbonization.