

POSTER

FURTHER STUDIES OF THE OXIDATION RESISTANCE OF CARBON-CARBON COMPOSITES PREPARED BY LIQUID PHASE IMPREGNATION/CARBONIZATION

S. Kokenes, P. A. Thrower and L. R. Radovic
Department of Materials Science and Engineering,
The Pennsylvania State University, University Park, PA 16802, USA

INTRODUCTION

In some recent work, we found that carbon-carbon composites made with porous, high-surface-area fibers and liquid matrix precursors were more resistant to oxidation than comparable composites made with non-porous, low-surface-area fibers [1]. The porous fibers were produced by an oxidative activation process. This created porosity and also modified the surface chemistry of the fibers. Either consequence of the activation process could be responsible for the observed improvements in oxidation resistance.

If the porosity is the controlling factor, then the oxidation resistance could arise from the following mechanisms. The liquid matrix precursor would flow into the pores, mechanically locking together the fiber and matrix [2]. This alone could serve by preventing large cracks from opening at the fiber-matrix interface. It is also possible that the increased constraint of the matrix precursor in the pores and at the interface would promote stress-graphitization of the matrix carbon [3]. This would reduce reactivity by the fact that more crystalline carbon is less reactive.

The surface chemistry could also be responsible for the improvements. If this is so, then adhesion of the matrix to the fibers could produce effects similar to those postulated in the porosity-controlled case. Fiber-matrix adhesion is a well known effect in polymer-matrix composites [4]. It is known that although the chemical bonding between the fibers and a polymeric matrix may not be conserved upon pyrolysis, the existence of that bonding will affect the final composite's microstructure [5].

The experiments described here were designed in an attempt to assess the relative importance of surface chemistry and porosity of the fibers for the resulting oxidation behavior of the composites.

EXPERIMENTAL

Carbon-carbon composites were produced using VCL fibers (Amoco) and two matrix precursors: A240 petroleum pitch (Ashland), and SC1008 phenol-

formaldehyde resin (Borden). The pitch-based composites were prepared by a pressure impregnation process at 2000 psi and 500 °C followed by a 1000 °C heat treatment at ambient pressure. The resin-based composites were cured and subsequently given the same 1000 °C heat treatment. Some composites were then heat-treated to 2850 °C.

Initially, the VCL fibers had been given certain treatments. These treatments were as follows: 1000 °C in inert atmosphere, activation in CO₂ at 850 °C to a level of 25% burnoff, and nitration for 30 minutes in hot concentrated HNO₃. The four categories of fiber were then: heat treated only (ut), activated then heat treated (at), activated then nitrated (an), and nitrated only (un).

The oxidation resistance of the composites was tested in flowing air in a Cahn 2000 TGA apparatus. The composites' crystal structure was investigated by X-ray diffraction (Rigaku Geigerflex). The composites were also examined with a scanning electron microscope.

RESULTS

The effect of the fiber surface treatments on the oxidation resistance of the composites is most visible in the 1000 °C samples (Figure 1). In composites from both matrix precursors, the (an) treatment appeared to have the largest effect on oxidation resistance. This was followed by the (un) treatment. In both cases, the composites made with (ut) fibers had the poorest oxidation resistance. This order of reactivity is repeated in the 2850 °C resin-matrix-precursor composites (Figure 2). The reactivities of the 2850 °C pitch-matrix-precursor composites are very similar regardless of fiber treatment.

The XRD experiments did not show any strong correlation between crystallinity and oxidation resistance (Table 1). The SEM experiments, however, appeared to show that the more oxidation-resistant composites had better fiber-matrix coupling and a thicker matrix layer around the fibers.

DISCUSSION

All composites except the high-temperature-treated pitch-matrix-precursor composites showed a consistent effect of the surface treatments. Generally, the composites made with fibers given the (an) treatment had superior oxidation resistance. When this is taken in conjunction with the apparent lack of a strong influence from crystallinity, it suggests that chemical adhesion is the dominant mechanism by which the oxidation resistance is improved. Clearly, the larger the surface area for adhesion to occur, the more pronounced is the effect.

ACKNOWLEDGMENT

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Table 1. XRD data for the composites studied.

Sample	d ₀₀₂ , Å	L _c , Å	L _a , Å
SP-1 graphite	3.34	158	399
vanpht	3.37	161	253
vunpht	3.38	158	252
vatpht	3.37	161	324
vutpht	3.38	155	219
vanrht	3.39	80	116
vunrht	3.37	143	72
vatrht	3.36	134	91
vutrht	3.38	149	83
vanplt	3.53	11	49
vunplt	3.49	11	51
vatplt	3.49	14	51
vutplt	3.54	13	60
vunrlt	3.95	-	38
vatrlt	3.86	-	43
vutrlt	4.04	-	43

Note: v = VCL fiber;
 a/u = activated/unactivated;
 n/t = nitrated/heat-treated;
 p/r = pitch/resin (matrix);
 lt/ht = 1000 °C/2850 °C (heat treatment).

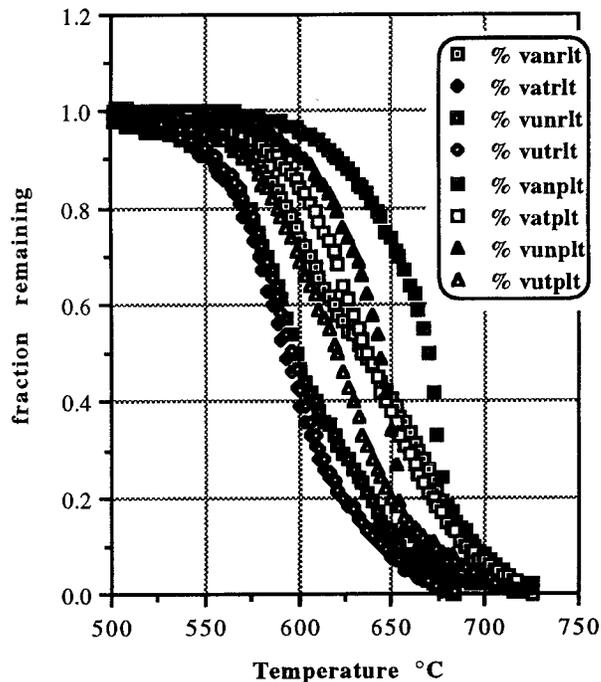


Figure 1. Burnoff of LT composites in air at a heating rate of 5 °C/min.

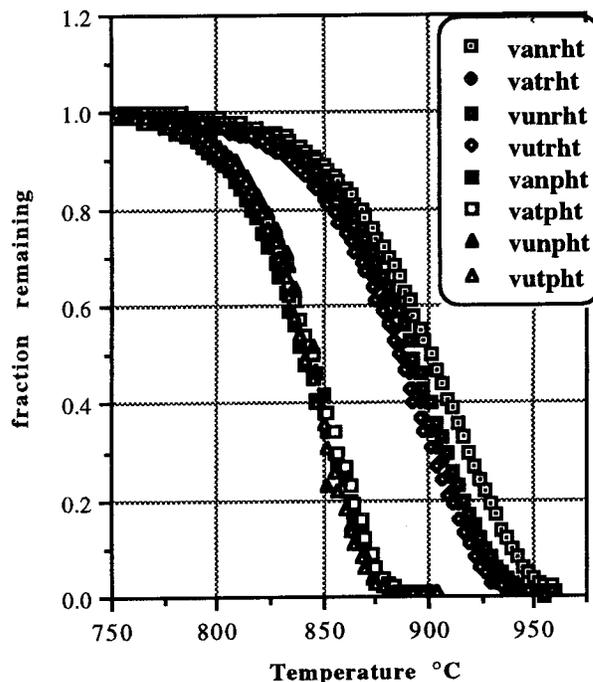


Figure 2. Burnoff of HT composites in air at a heating rate of 5 °C/min.