STUDY OF OXIDATION OF CARBON FIBERS USING RESISTANCE MEASUREMENT

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Introduction

The poor oxidation resistance of carbon fibers (CFs) has limited their wider applications in high temperature environment and much research has been carried out to study the oxidation behavior of CFs [1] and to prevent the oxidation problem [2]. For the investigation of oxidation of CFs, thermogravimetric analysis (TGA) is a useful and frequently used quantitative analysis technique to study the oxidation kinetics and mechanism. In the present work, an alternative method involving the resistance measurement of CFs during oxidation was proposed to study the oxidation behavior of CFs. The experimental results were compared with those obtained by TGA and a comparison between these two techniques is discussed.

Experimental

The PAN-based CFs (TC-33) used in the oxidation study are 3k fiber tows produced by Formosa Plastics Corporation, Taiwan. Both as-received and 2300℃ heat-treated CFs were investigated. Figure 1 shows the experimental setup for the resistance measurement of CF tows during oxidation. A small home-made quartz tube furnace (inside diameter = 1.2 cm, length = 15 cm) was used to oxidize the CF under the ambient condition. The two ends of the CF tow were fixed outside the tube furnace using the copper blocks, where the resistance of the CF tow was measured using a Keithley model 580 micro-ohmmeter. Temperature calibration indicated that the uniform temperature zone (±3℃) was less than 1 cm. Therefore, for the observation of morphology after oxidation, samples were taken from this zone. For the oxidation test at the specific temperature (300~700℃), the sample was heated at a rate of 50℃/min to that temperature and maintained at that temperature for 3 hrs. Non-isothermal and isothermal TGA were carried out in air at a flow rate of 60 ml/min. The heating rate for non-isothermal TGA was 5℃/min. For the isothermal TGA, samples were heated to the desired temperature in argon prior to the introduction of air.

Results and Discussion

Figure 2 shows the variation in resistance with time during oxidation at different temperatures for both as-received and 2300℃ heat-treated CFs. As shown in Fig. 2, the decrease in resistance with time at the beginning of the oxidation test is due to the temperature increase, and the increase in resistance with time at the end of the oxidation test is due to the temperature decrease, which indicates the semiconductor characteristics of CFs. For the as-received CFs (Fig. 2(a)), the resistance remained constant during the oxidation test at 300℃, indicating that no oxidation occurred. At oxidation temperatures of 400 and 500℃, the increase in resistance was measured and a greater increase was found for the higher oxidation temperature. These results suggested that oxidation began at 400℃ and the extent of oxidation increased with oxidation temperature. Sever oxidation was found when the oxidation temperature was raised to 600℃. A very rapid increase in resistance to the measurement limit (200 kΩ) of the equipment was observed after about 100 min of oxidation at 600℃, suggesting that the fiber tow was broken due to oxidation. For the 2300℃ heat-treated CFs, as shown in Fig. 2(b), oxidation began at a higher temperature (500~600℃) than that of as-received CFs due to the higher structural perfection [3]. At 500 and 600℃, only a small increase in resistance was measured. As the temperature was raised to 700℃, severe oxidation was found after about 50 min of oxidation with a very rapid increase in resistance to the measurement limit (200 kΩ) of the equipment. The increase in the rate of resistance was much higher than that of as-received CFs at 600℃, presumably due to the higher oxidation temperature.

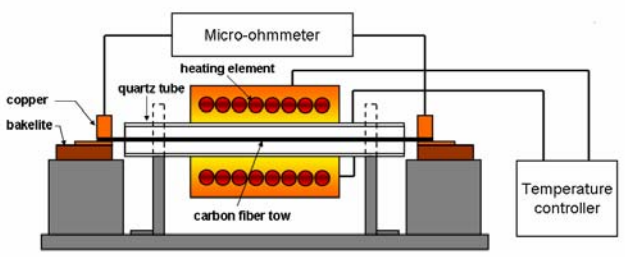

Fig. 1 Experimental setup for the resistance measurement of carbon fibers during oxidation.

TGA was also performed under an air atmosphere to confirm the above resistance measurement results. Figure 3 shows the non-isothermal TGA results of both as-received and 2300℃ heat-treated CFs. The oxidation resistance was improved after 2300℃ heat treatment as expected although the improvement was small due to the non-graphitizable nature of PAN-based CFs. To further assess the oxidation resistance at constant temperature, isothermal TGA was also performed and the results are presented in Fig. 4. For as-received CFs, a weight loss of only about 0.24% at oxidation temperature of 300℃ (solid line (a)) was observed after 2 hrs and the weight approached a near constant relatively quickly. On the other hand, about 1.3% weight loss was measured at 400℃ (solid line (b)) and a steady state weight loss was observed, suggesting that slight oxidation began. The above TGA results are qualitatively consistent with those obtained by the resistance measurements. For the 2300℃ heat-treated

CFs, only about 0.5% weight loss at an oxidation temperature of 400℃ (dashed line (c)) was observed after 2 hrs and 4.5% weight loss was obtained at 500℃ (dashed line (d)), which is also qualitatively consistent with the resistance measurements. On comparing isothermal TGA and resistance measurement results at 400℃, it is found that both indicate that CFs heat treated at 2300℃ show better oxidation resistance than as-received CFs. However, it must be mentioned that the increase in resistance resulting from fiber oxidation is not necessarily proportional to the fiber weight loss for different fibers. For example, the weight loss of 2300℃ heat-treated CFs at 500℃ (4.5%) is larger than that of as-received CFs at 400℃(1.3%), but as-received CFs showed a slightly higher increase in resistance. Different oxidation behaviors, for example uniform oxidation or pitting, might cause different degrees of increase in resistance.

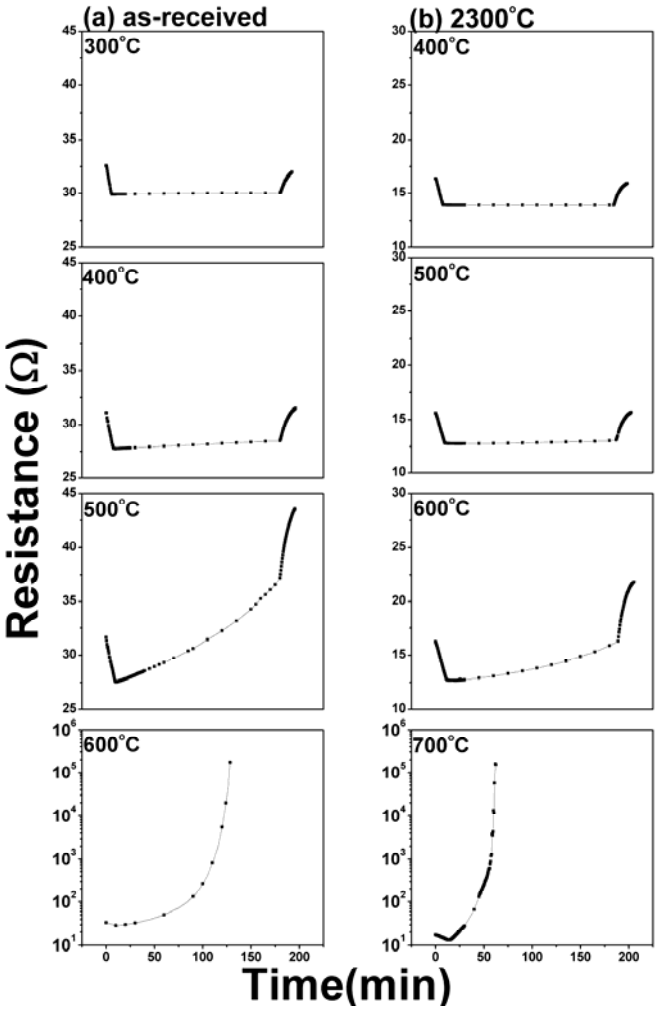

Fig. 2 Variation in resistance with time during oxidation at different temperatures for: (a) as-received CFs and (b) 2300℃ heat-treated CFs.

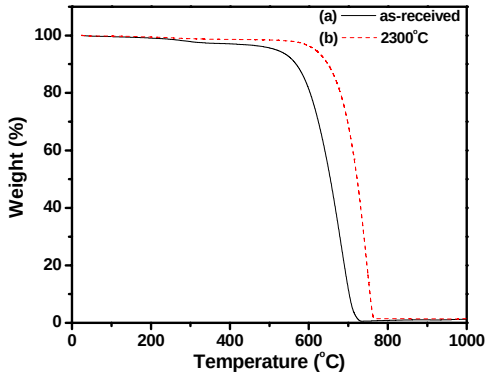

Fig. 3 Non-isothermal TGA analyses of CFs: (a) as-received CFs and (b) 2300℃ heat-treated CFs.

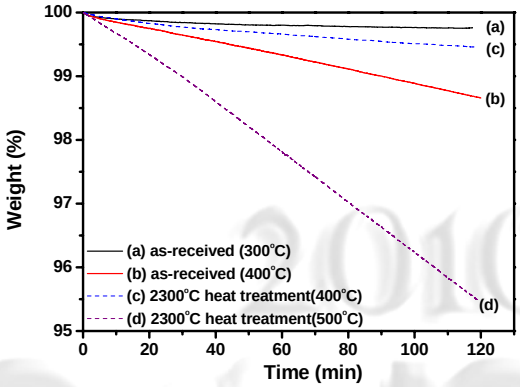

Fig. 4 Isothermal TGA analyses of as-received and 2300℃ heat-treated CFs at different temperatures: (a) as-received CFs, 300℃, (b) as-received CFs, 400℃, (c) 2300℃ heat-treated CFs, 400℃ and (d) 2300℃ heat-treated CFs, 500℃.

Conclusions

An alternative method involving the resistance measurement of CFs during oxidation is proposed to study the oxidation behavior of CFs, which might also be applied to other carbon materials. The experimental results from resistance measurements at different oxidation temperatures show qualitative consistency with those obtained using the TGA technique for the same type of fiber. Refinement of the experimental setup and more experimental data and analysis are needed for more quantitative study of fiber oxidation.

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References

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