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# Study of Oxidation of Carbon Fibers Using Resistance Measurement

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**Thermogravimetric analysis (TGA) is a useful and frequently used quantitative analysis technique to study the oxidation kinetics and mechanism of carbon fibers (CFs). An alternative method involving the resistance measurement of CFs during oxidation is proposed to study the oxidation behavior of CFs in this study, which might be also applied to other carbon materials. 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. A comparison between these two techniques is discussed.**

**Keywords** carbon fibers, oxidation, resistance

## 1. Introduction

Carbon fibers (CFs) are widely used as reinforcement in advanced composite materials due to the excellent properties, such as high specific strength and modulus, low thermal expansion, and high thermal conductivity. However, the poor oxidation resistance of CFs, besides the cost, has limited their wider applications in high-temperature environment since a significant reduction in mechanical properties of the composites will result once the interface between fiber and matrix has been debonded by oxidation (Ref 1). Therefore, much research has been carried out to study the oxidation behavior of CFs (Ref 2, 3) and to prevent the oxidation problem (Ref 4, 5). 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.

## 2. 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 °C heat-treated CFs were investigated. The heat treatment at 2300 °C was carried out in a Centorr graphite furnace under an argon atmosphere. The heating rate was 250 °C/h above 900 °C and the hold time was 1 h. 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 °C) 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 °C), the sample was heated at a rate of 50 °C/min to that temperature and maintained at that temperature for 3 h. 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 °C/min. For the isothermal TGA, samples were heated to the desired temperature in argon prior to the introduction of air.

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## 3. Experimental Results and Discussion

Figure 2 shows the variation in resistance with time during oxidation at different temperatures for both as-received and 2300 °C 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. 2a), the resistance remained constant during the oxidation test at 300 °C, indicating that no oxidation occurred. At oxidation temperatures of 400 and 500 °C, 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 °C and the extent of oxidation increased with oxidation temperature. Severe oxidation was found when the oxidation temperature was raised to 600 °C. 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 °C, suggesting that the fiber tow

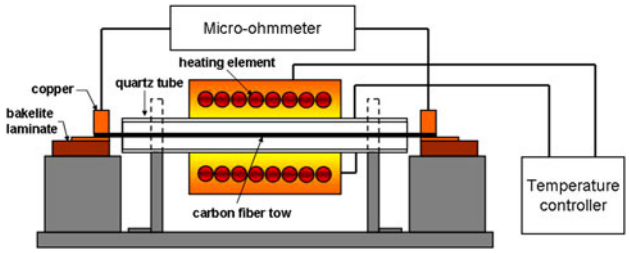


**Fig. 1** Experimental setup for the resistance measurement of carbon fibers during oxidation

was broken due to oxidation. For the 2300 °C heat-treated CFs, as shown in Fig. 2(b), oxidation began at a higher temperature (500-600 °C) than that of as-received CFs due to the higher structural perfection (Ref 6). At 500 and 600 °C, only a small increase in resistance was measured. As the temperature was raised to 700 °C, 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 °C, presumably due to the higher oxidation temperature. In Fig. 2, the resistance was only recorded to ~100 °C after cooling and the resistance after

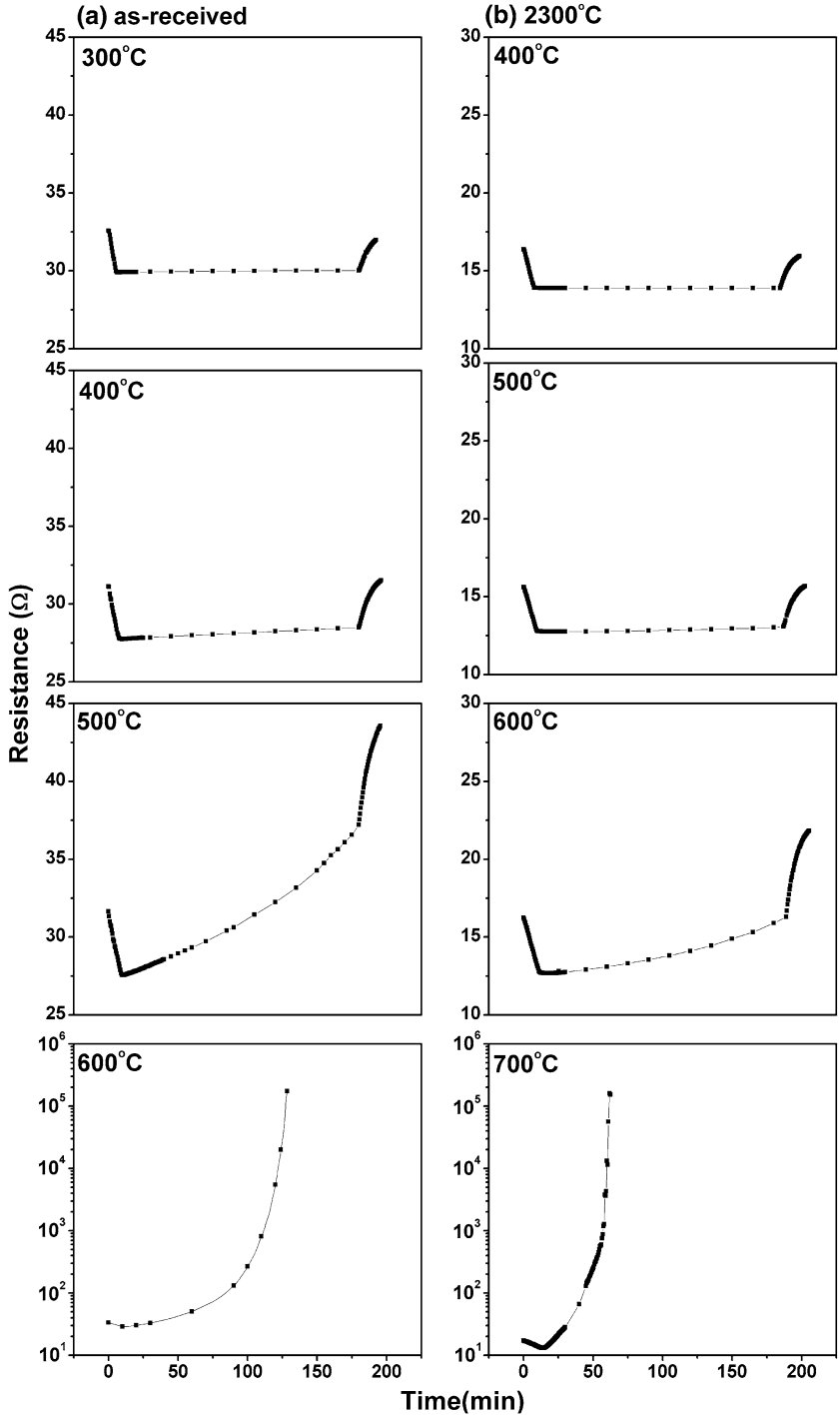


**Fig. 2** Variation in resistance with time during oxidation at different temperatures for (a) as-received CFs and (b) 2300 °C heat-treated CFs

**Table 1 Variation in resistance during oxidation test**

| Fiber type | Oxidation temperature, °C | Resistance, Ω (a) At the beginning | (b) Start of oxidation temperature | (c) End of oxidation temperature | (d) Cooling to room temperature | Resistance change [(c) − (b)]/(b), % | Resistance change [(d) − (a)]/(a), % |
|---|---|---|---|---|---|---|---|
| As-received CFs | 300 | 32.57 | 29.89 | 30.02 | 32.70 | 0.43 | 0.40 |
| | 400 | 31.13 | 27.77 | 28.50 | 32.18 | 2.63 | 3.37 |
| | 500 | 31.64 | 27.67 | 37.20 | 44.97 | 34.44 | 42.13 |
| 2300 °C heat-treated CFs | 400 | 16.38 | 13.93 | 13.88 | 16.39 | −0.36 | 0.06 |
| | 500 | 15.61 | 12.83 | 13.08 | 16.13 | 1.95 | 3.33 |
| | 600 | 16.25 | 12.76 | 16.29 | 22.17 | 27.66 | 36.43 |

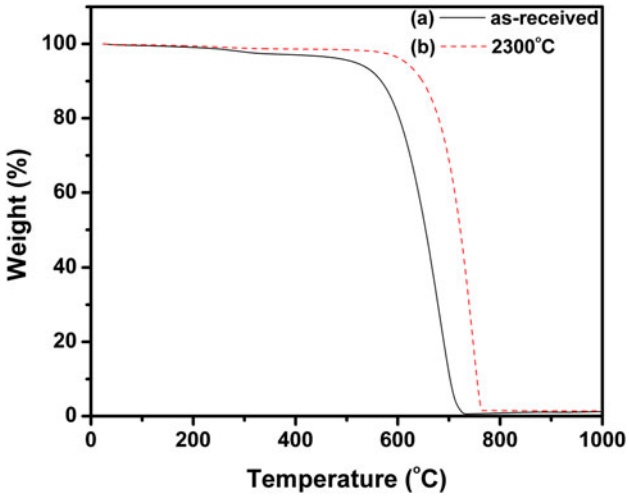


**Fig. 3** Non-isothermal TGA analyses of CFs: (a) as-received CFs and (b) 2300 °C heat-treated CFs

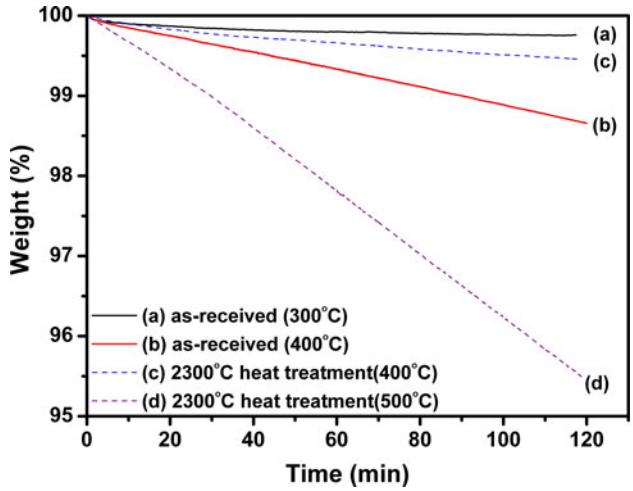


**Fig. 4** Isothermal TGA analyses of as-received and 2300 °C heat-treated CFs at different temperatures: (a) as-received CFs, 300 °C; (b) as-received CFs, 400 °C; (c) 2300 °C heat-treated CFs, 400 °C; and (d) 2300 °C heat-treated CFs, 500 °C

cooling to the room temperature is presented in Table 1. It is clear that both the resistance for 300 °C oxidation of as-received CFs and the resistance for 400 °C oxidation of 2300 °C heat-treated CFs returned very closely to the initial values before the oxidation test, which further proves that almost no oxidation occurred. The detailed resistance change during the oxidation test is also presented in Table 1. It is noted that the percentage of resistance change calculated using the values measured at the room temperature and the percentage of resistance change calculated using the values measured at the oxidation temperature show the same trend. It is also noted that the initial resistance (∼16 Ω) of 2300 °C heat-treated CFs is smaller than that (∼32 Ω) of as-received CFs due to the higher structural perfection.

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 °C heat-treated CFs. The oxidation resistance was improved after 2300 °C 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 °C (solid line (a)) was observed after 2 h and the weight approached a near constant relatively quickly. On the other hand, about 1.3% weight loss was measured at 400 °C (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 °C heat-treated CFs, only about 0.5% weight loss at an oxidation temperature of 400 °C (dashed line (c)) was observed after 2 h and 4.5% weight loss was obtained at 500 °C (dashed line (d)), which is also qualitatively consistent with the resistance measurements. On comparing isothermal TGA and resistance measurement results at 400 °C, it is found that both indicate that CFs heat treated at 2300 °C 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 °C heat-treated CFs at 500 °C (4.5%) is larger than that of as-received CFs at 400 °C (1.3%), but as-received CFs showed a slightly higher increase in resistance (Table 1). Different oxidation behaviors, for example uniform oxidation or pitting, might cause different degrees of increase in resistance.

The SEM photographs of CFs after oxidation at different temperatures are presented in Fig. 5. For the as-received CFs (Fig. 5a and b), oxidation at 400 °C occurred preferentially at the groove of surface striation, and the width of the groove became larger after 500 °C oxidation. A different oxidation

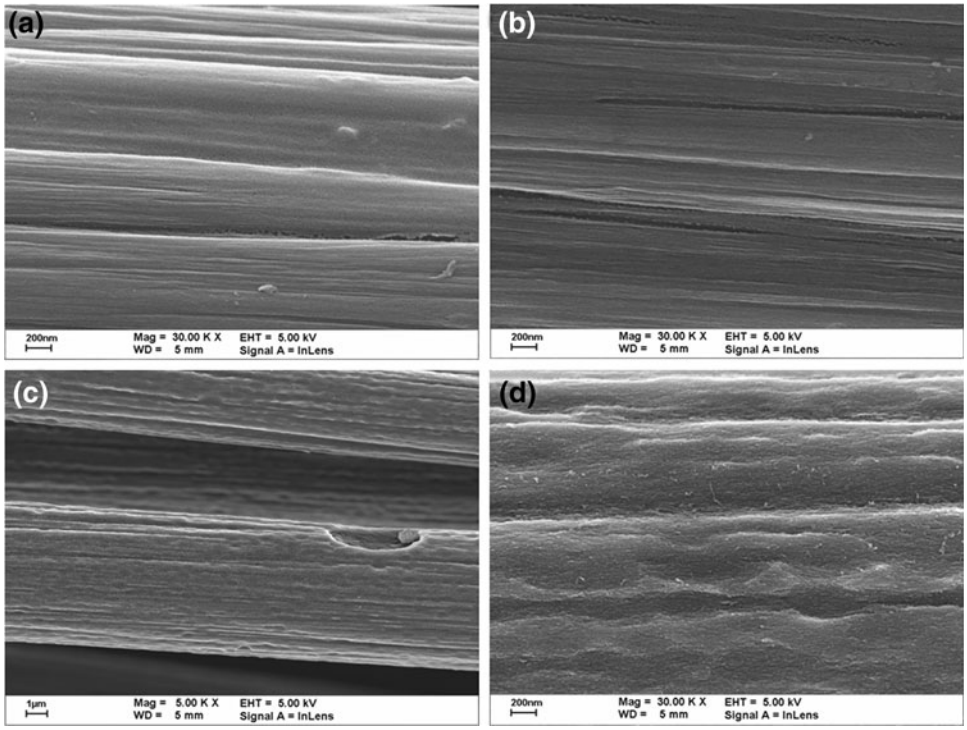


**Fig. 5** SEM photographs of CFs oxidized at different temperatures: (a) as-received CFs, 400 °C; (b) as-received CFs, 500 °C; (c, d) 2300 °C heat-treated CFs, 600 °C

morphology was observed for the 2300 °C heat-treated CFs. At 500 °C, no obvious morphology change could be found in spite of the very slightly increase in resistance. Oxidation at 600 °C (Fig. 5c and d) occurred randomly from all over the surface and the surface roughening can be observed. Larger pitting was also observed for the 2300 °C heat-treated CFs oxidized at 600 °C (Fig. 5c), which was not found for as-received CFs even after oxidization at 600 and 700 °C.

Some differences in the oxidation condition between the TGA technique and the present resistance measurement must be mentioned. In the resistance measurement of the current experimental setup, only the central portion (about 1 cm) of the CF tow positioned in the middle of the furnace is at the desired oxidation temperature, whereas in the TGA, the entire sample is at the oxidation temperature. This non-uniform temperature oxidation condition may restrict its use only in the qualitative assessment. Also, as discussed previously, the increase in resistance from fiber oxidation is not necessarily proportional to the fiber weight loss, especially for different fibers with different oxidation behaviors and different microstructures, which further restricts its quantitative capability in the oxidation study. On the other hand, the fiber sample in the TGA has a lower aspect ratio and the fiber could be oxidized from both the surface and the end. However, using the resistance measurement, the fiber is oxidized mainly from the surface. Therefore, different results might be obtained if the fibers have different oxidation rates in these two locations, for example the vapor-grown CFs with an onion-type transverse microstructure and CFs with a skin-core microstructure considering the difference in the oxidation activity in the edge plane and the basal plane of graphite crystals. In this sense, the resistance measurement technique could be used to explore these characteristics. Another capability of resistance measurement is that it could be applied to other carbon materials with larger dimensions. In situ study of oxidation using resistance measurement is also possible.

## 4. Conclusions

In summary, 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.

### Acknowledgment

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### References

1. T.A. Bullions, J.E. McGrath, and A.C. Loos, Thermal-Oxidative Aging Effects on the Properties of a Carbon Fiber-Reinforced Phenylethynyl-Terminated Poly(etherimide), *Compos. Sci. Technol.*, 2003, **63**, p 1737–1748
2. D.W. McKee and V.J. Mimeault, Surface Properties of Carbon Fibers, *Chemistry and Physics of Carbon*, P.L. Walker, Jr., and P.A. Thrower, Ed., Marcel Dekker, Inc., NewYork, 1973, p 151–245
3. L.M. Manocha, A. Warrier, S. Manocha, D.D. Edie, and A.A. Ogale, Oxidation Behavior of Ribbon Shape Carbon Fibers and Their Composites, *Mater. Sci. Eng. B*, 2006, **132**, p 121–125

4. Y.J. Lee and L.R. Radovic, Oxidation Inhibition Effects of Phosphorus and Boron in Different Carbon Fabrics, *Carbon*, 2003, **41**, p 1987–1997
5. Z.J. Dong, X.K. Li, G.M. Yuan, Y. Cong, N. Li, Z.W. Hu, Z.Y. Jiang, and A. Westwood, Fabrication of Protective Tantalum Carbide Coatings on Carbon Fibers Using a Molten Salt Method, *Appl. Surf. Sci.*, 2008, **254**, p 5936–5940
6. M.S. Dresselhaus, G. Dresselhaus, K. Sugihara, I.L. Spain, and H.A. Goldberg, *Graphite Fibers and Filaments*, Springer-Verlag, Berlin, 1988, p 240