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Effect of polymeric precursors on properties of semiconducting carbon/carbon composites

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Microstructure, oxidation behaviour, and electrical and mechanical properties of quasi-carbon fibre-reinforced quasi-carbon matrix (QC/QC) composites were investigated. The composite was prepared by heat treating a QC fibre or OXPAN fibre-reinforced polymer matrix composite at a temperature of 500 °C. Different polymer precursors have resulted in the QC/QC composites with varying thermal behaviour. The phenolic matrix derived QC/QC composites followed a self-acceleration mechanism and had better oxidation resistance than the polyacrylonitrile (PAN) matrix-derived QC/QC composites. Because of fewer chemical reactions involved in the pyrolysis process, the QC/QC composites obtained from QC fibre-reinforced composite precursors exhibited higher flexural modulus and strength and were superior to those derived from oxidized PAN (OXPAN) fibre-reinforced composite precursors. Unique semiconducting and switching characteristics have been observed in the QC/QC composites, which would make them promising for electronic device applications.

1. Introduction

The study of carbon/carbon (C/C) composites has been of interest for more than 30 years. The fabrication of a conventional C/C composite is usually involved in a process that heat treats a carbon fibre-reinforced polymer (e.g. phenolic and pitch) matrix composite as a precursor at a temperature of 950–1400 °C, then graphitizes it at a temperature up to 2800 °C [1–4]. Thus, many unique properties of C/C composites, such as high thermal stability, high strength and stiffness in high temperature, and good compatibility with the tissue, have made them attractive for aerospace, automotive and medical applications. However, other areas of applications may need to develop a material with other unique chemical and physical behavior while maintaining these good thermal and mechanical properties. Semiconducting C/C composite is expected to be a good example of these types of materials.

The production of the semiconducting C/C composite may follow a similar process used for fabricating the conventional C/C composite. With the proper control of the heat-treatment temperature (HTT) below 900 °C (e.g. 500–600 °C), the fibres and the polymer matrix in the composite are converted to a partially carbonized state, thus exhibiting a semi-conducting characteristic. Such a composite in the current study is referred to as the quasi-carbon fibre-reinforced quasi-carbon matrix (QC/QC) composite. In principle, two types of fibre-reinforced polymer matrix composites can be utilized to produce QC/QC composites: (1) polymeric fibre-reinforced composite; (2) partially carbonized fibre (i.e. QC fibre)-reinforced composite. For the former, during the fabrication process of the composite, the partial carbonization simultaneously converts both the polymeric fibres and the polymeric matrix into the QC state whereas in the latter case, only the matrix is partially carbonized because the fibre component was already in a QC state and may be less chemically active (unless the HTT exceeds the original HTT which the QC fibres have experienced). An example of the first category is the polyacrylonitrile (PAN) fibre or the oxidized polyacrylonitrile (OXPAN) fibre-reinforced phenolic matrix composite. The OXPAN/phenolic composite as the QC/QC composite precursor has been studied by several research groups [5–7]. Markovic *et al.* [5], in pyrolysing the precursor with a HTT of 300 ∼ 1000 °C, revealed that the simultaneous partial carbonization could weaken the fibre/matrix adhesion, leading to the destruction of the fibre materials. Ko *et al.* [6] also concluded that the vigorous chemical reactions occurring at the

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fibre/matrix interface during the pyrolysis of OX-PAN/phenolic composite impaired interfacial bonding and resulted in the deterioration of the mechanical properties in the resulting QC/QC composite. Hence, the utilization of the QC fibres as the reinforcement in the composite precursor will possess an advantage over that of the OXPAN fibre because the QC fibres would be relatively inert to the pyrolysis process. In most of the cases studied, a carbon matrix in the C/C composite or a quasi-carbon matrix in the QC/QC composite was derived from phenolic or pitch matrix; however, according to a recent report [8], the PAN resin could be another possible source because it has also been successfully converted into the partially carbonized stage. Therefore, in this paper, both phenolic and PAN matrix composites reinforced with the QC fibres or the OXPAN fibres will be investigated. A comparative study on microstructure, thermal behaviour, and electrical and mechanical properties of QC/QC composites derived from these various precursors would give an improved understanding in process–structure–property relationship of carbon-based composites, and help shed some light on the exploration of their unique properties for electronic applications.

2. Experimental Procedure

2.1. Materials

Starting materials selected in this study are: (1) PAN fibres (6K strands, each 1.1 denier and 11.5 μm in average diameter) provided by RK Carbon Fibre, Inc.; (2) resol-type phenolic resin (MXR-6055) supplied by ICI Fiberite; and (3) PAN resin (BAREX) supplied by BP Chemicals. Both of them were used as the matrix for the preparation of OXPAN fibre- or QC fibre-reinforced phenolic and PAN matrix composites. The OXPAN fibres were obtained by the stabilization of the PAN fibres at a temperature range of 210 ~ 230 °C for 3 h, and the QC fibres were fabricated by pyrolysing the OXPAN fibres with a HTT of 500 °C for 1 h [9–10]. The main properties of OXPAN fibres and QC fibres are summarized in Table I.

2.2. Preparation of PAN or phenolic matrix composites

Two steps were involved in the preparation of unidirectional PAN and phenolic matrix composites. The first one was the use of the impregnation technique to obtain the prepregs which were then subjected to a curing process to produce composites. Thus, the phenolic resin was diluted to form a 50% ethyl alcohol solution which impregnated the aligned OXPAN fibres or QC fibres in the form of tows with 6K strands to obtain unidirectional OXPAN fibre– or QCF–phenolic resin prepregs by converting the impregnated fibres into the "B" stage. The process was accomplished by heating at 80 °C for 6 min and subsequently drying under a vacuum for 24 h. A similar procedure was followed to prepare unidirectional OXPAN fibre– or QC fibre–PAN resin prepregs where a 30% PAN solution in *N*,*N*-dimethyl formamide (DMF) was used. The impregnated fibres were stuck to a thin PAN film which was obtained by the extrusion process, then evaporated and dried under a vacuum at room temperature for 48 h.

TABLE I Main properties of OXPAN fibres and QC fibres

Properties	OXPAN fibres	QC fibres
Diameter (μm)	11.00	9.40
Density ($g\,cm^{-3}$)	1.37	1.61
Bragg's 2θ (degree)	24.4	25.0
Half-peak width (degree)	13.2	7.6
Stacking size (L_c, nm)	0.685	1.190
Tensile strength (MPa)	184.9	134.4
Tensile modulus (GPa)	6.43	39.84
Ultimate elongation (%)	16.42	0.339
Electrical resistivity (log ρ, Ω cm)	> 10	3.736

Unidirectional composites with a fibre volume fraction (V_f) of approximately 42% were produced in a rectangular shape with 6.5 × 1.2 cm in length and width. Thickness of the laminates was about 0.15 cm, which varied with the fibre and resin types because of the density difference. In order to make the resulting composites comparable, the same amount of fibre bundles in the form of prepregs was used in each composite. Thus, the prepregs were cut into the desired geometry, stacked together at 0° direction in a rectangular mould and cured by a hot-pressing technique. The PAN matrix composites were obtained by the compression moulding process at 170 °C for 15 min under an air pressure of 4 MPa (Fig. 1), and the phenolic matrix composites followed a step-wise curing process as shown in Fig. 2. The void content was estimated by scanning electron microscopy (SEM) to be less than 5% and 10% for the PAN and phenolic composites, respectively.

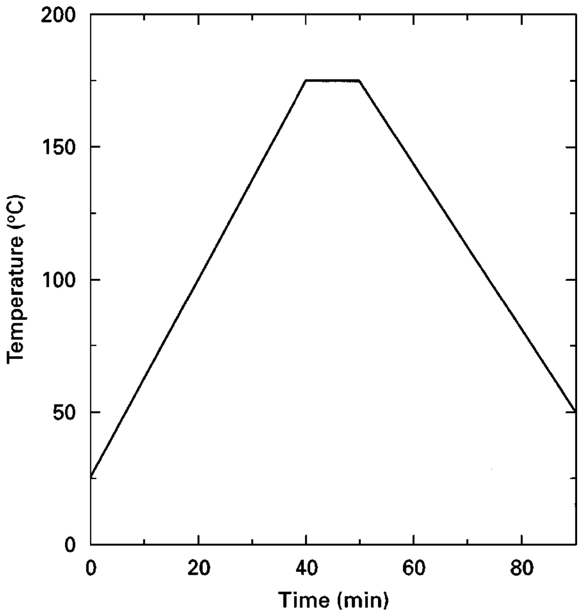


Figure 1 Curing process for the fabrication of PAN matrix composites.

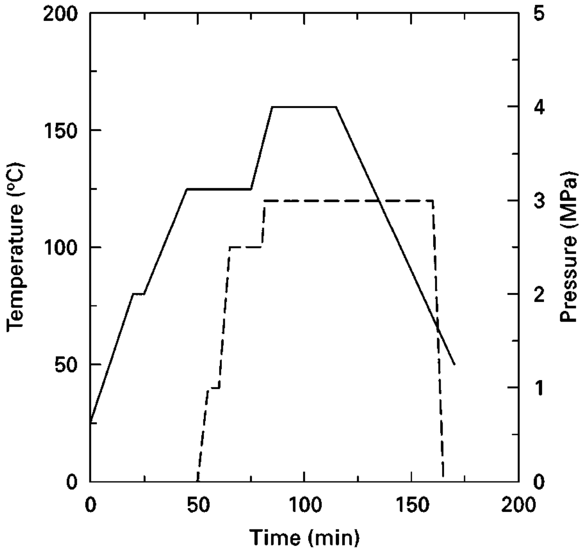


Figure 2 Curing process of the fabrication of phenolic matrix composites. (——) Temperature; (– – –) pressure.

2.3. Fabrication of QC/QC composites

There were four polymer composite precursors used to produce the QC/QC composites by pyrolysis at a desired temperature in an argon atmosphere: (a) QC fibre/phenolic composite; (b) QC fibre/PAN composite; (c) OXPAN fibre/phenolic composite; and (d) OXPAN fibre/PAN composite. Fig. 3 schematically illustrates the fabrication procedure of the QC/QC composite. With the current processing practice, the first three precursors have been successfully converted into the QC/QC composite which will be discussed in following sections. The fabrication process was completed by heat treating either OXPAN fibre- or QC fibre-reinforced composite precursors at a HTT of 500 °C in an argon atmosphere for 1 h with the heating rate of 2 °C min^{-1}. The specific HTT of 500 °C was selected in producing QC/QC composites because partially carbonized products prepared at this HTT were found to have unusual electrical properties [11]. After the process, a large pyrolysis-induced volume shrinkage in these QC/QC composites was observed. The strong chemical reactions between the OXPAN fibres and the PAN matrix during the partial carbonization were considered to be the cause for obtaining a C/C composite with considerable amount of cracks in its surface. The composite was not tested further.

2.4. Characterization techniques

The density (d) of composites was measured by the density gradient column method as specified by ASTM D1505. A density gradient of 0.867–1.989 g cm^{-3} was obtained in a 1.10 m long glass tube by using a mixture of toluene and 1,3-dibromopropane. Five small cubic pellet specimens cut from each composite sample were used to obtain the average density value.

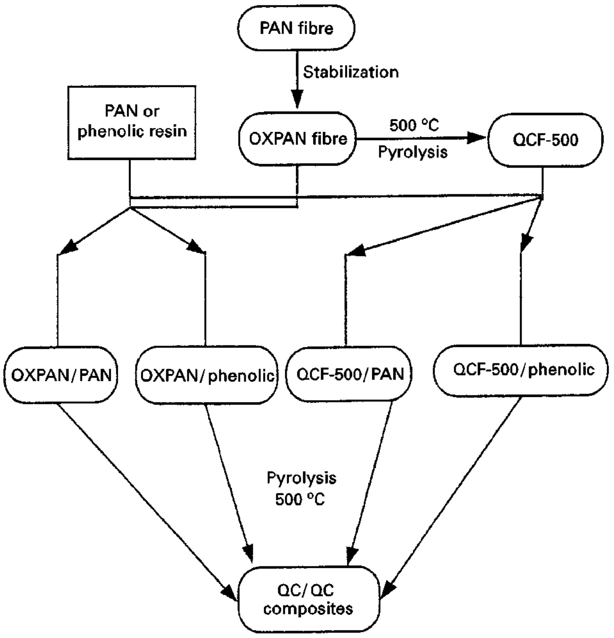


Figure 3 Schematic illustration of the fabrication procedure for QC/QC composites.

The microstructure of composites was determined by a Rigaku model wide-angle X-ray diffractometer (XRD) with a CuK$_\alpha$ radiation source. The stacking size (L_c) of samples was calculated from the half-peak width (B) of the (0 0 2) reflection, using the well-known Scherrer equation (Equation 1)

$$L_c = k\lambda/B\cos\theta \qquad (1)$$

where $\lambda = 0.154$ nm, θ is the Bragg's angle and k is a constant (ca. 1.0).

A Perkin-Elmer TGA-7 (thermogravimetric analysis) was employed for studying the oxidation behaviour of QC/QC composites. The weight loss of materials was determined by the TGA microbalance with a sensitivity of 0.001 mg. The composite sample was cut into a small cube of about 10 mg and then placed in a platinum sample holder. Both dynamic and isothermal thermogravimetric scans were performed, using an air flow rate of 80 ml min^{-1}. The dynamic TGA scan was carried out with a heating rate of 20 °C min^{-1} from 50 to 1200 °C, while the isothermal TGA scan was conducted in a temperature range from 450 to 550 °C. The activation energy (Q) of materials and the pre-exponential constant (r_0) for the oxidation can be attainable by using the Arrhenius equation (Equation 2)

$$r = r_0 \exp(-Q/kT) \qquad (2)$$

where r is the oxidation rate defined as dm/dt, the first derivative of the mass loss and k is the Boltzmann constant.

Mechanical properties of composites were measured with an Instron testing machine by conducting the flexural or three point bending test as specified by ASTM D790 with the sample support span (L) being 40 mm, the support span-to-depth ratio (L/d) 16/1 and a crosshead rate of 1.0 mm min^{-1}. At least five specimens for each composite sample were tested to obtain an average value of flexural strength (S) and modulus (M) according to Equations 3 and 4, respectively

$$S = 3PL/2bd^2 \qquad (3)$$

$$M = L^3m/4bd^3 \qquad (4)$$

where P is the maximum load, m is the slope of tangent to the initial straight-line portion in the flexural testing curve, and b and d stand for the specimen width and thickness, respectively.

The standard four-point method with a Hewlett-Packard (HP) Model-3497A constant current source was employed to measure the electrical resistance of composites with silver or aluminum as electrodes. Typical effective length of the QC/QC composite sample for the electrical measurement was 2 cm. The resistivity (ρ) was determined by the following equation

$$\rho = 2\pi LR \tag{5}$$

where R is the measured resistance determined from V/I data, L is the distance between two voltage probes. The pyroresistance effect was measured in the temperature range from 30 to 125 °C to determine the activation energy (E_a) for the conduction of semiconducting materials according to Equation 6.

$$\ln \rho = \rho_0 + E_a/kT \tag{6}$$

where ρ_0 is a material constant. A HP Model-4245A semiconductor parameter analyser with a d.c. source was also utilized to obtain a characteristic I–V curve of semiconducting QC/QC composites with an effective measurement length of 0.1–0.2 cm.

3. Results and discussion

3.1. Basic features

Table II shows the basic features of QC/QC composites in comparison with those of their precursors. Because of the density difference of fibre reinforcements, QC fibre-reinforced composites had a larger density value than the OXPAN fibre-reinforced composite. The three-dimensional network morphology of phenolic matrix has led to the QC fibre/phenolic composite with a more densified structure than its PAN matrix counterpart. After the partial carbonization, the density value of all samples was increased. More densified precursor also produced a more densified QC/QC composite, and vice versa. Thus, the QC/QC composite derived from the QC fibre/phenolic precursor (a) had the highest density value while that from the OXPAN fibre/phenolic precursor (c) showed the lowest value. As a result, both the QCF/phenolic precursor and its resulting QC/QC composite had a more compact structure. The various composite precursors also brought about different degrees of volume shrinkage during the process. Since the pyrolysis only converted the polymer matrix component to the QC state in precursor (a) and (b), a smaller volume change has been observed in these two composites. In contrast, the process would simultaneously convert both the fibres and the matrix in the OXPAN fibre/phenolic composite to the QC stage with an involvement of strong chemical reactions, thus, leading to a larger volume shrinkage. In such a QC/QC composite which was characterized with more defects in the turbostratic carbon structure, the homogeneous morphology was also observed as seen in Fig. 4, an SEM photograph taken from the texture of the OXPAN fibre/phenolic derived QC/QC composite, where the fibres and the matrix have been fused together and were difficult to identify.

TABLE II Basic features of QC/QC composites and their precursors

Composites	Density ($\mathrm{g\,cm^{-3}}$)	Volume shrinkage during pyrolysis (%)
(a) QCF-500/phenolic	1.455	–
(b) QCF-500/PAN	1.325	–
(c) OXPAN fibre/phenolic	1.306	–
QC/QC-500 composites derived from		
(a)	1.485	19.9
(b)	1.390	15.4
(c)	1.332	27.1

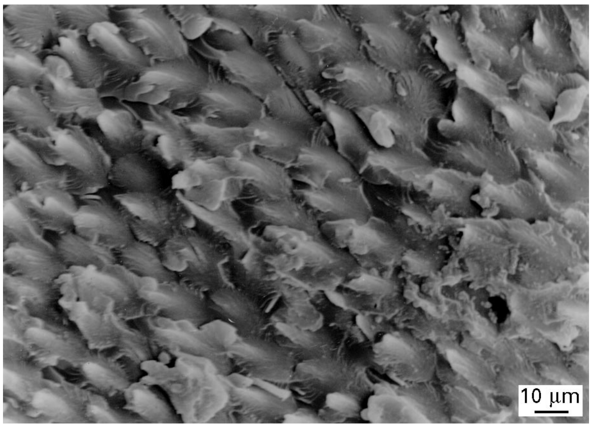


Figure 4 A SEM photograph for texture of the QC/QC composite derived from the OXPAN fibre/phenolic precursor (× 600).

3.2. Microstructure

The XRD pattern of all precursors, as demonstrated in Fig. 5, showed a peak at $2\theta \approx 25^\circ$ which was originated from the (0 0 2) diffraction of the fibre component. After the partial carbonization at 500 °C, the peak became more intensified with the decreasing half-peak width (B), indicating that the turbostratic carbon structure in the matrix was formed. The completion of such a partial carbonization conversion can be further verified by the fact that disappearance of the peak at $2\theta \approx 17^\circ$ which is corresponding to a characteristic reflection of the small crystallines of the PAN matrix in the QC fibre/PAN composite precursor. Because of the completely amorphous nature of the phenolic resin, no diffraction peak related to the matrix was found in the composite precursors. It has been observed that the value of half-peak width (B) and the stacking size (L_c) in QC/QC composites differed from various precursors. The smaller B value or the larger stacking size in the QC/QC composite derived from the QC fibre/PAN composite precursor indicated that the PAN matrix was easier to form the turbostratic carbon structure than the phenolic

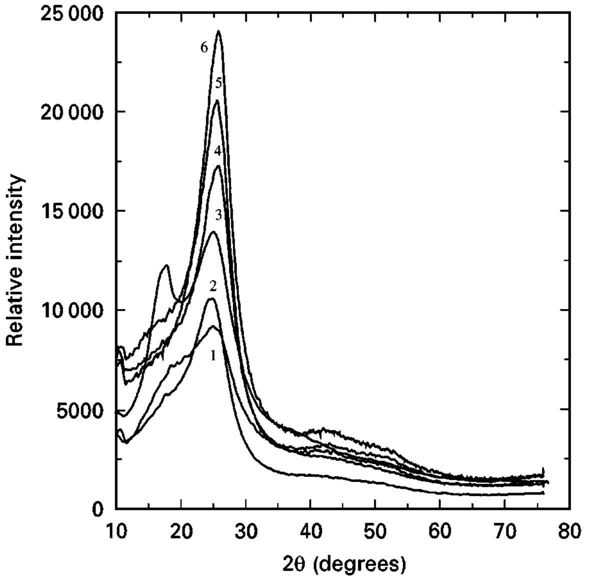


Figure 5 X-ray diffraction patterns: (1) OXPAN fibre/phenolic composite; (2) QC fibre/phenolic composite; (3) QC fibre/PAN composite; (4) QC/QC composites derived from (1); (5) QC/QC composites derived from (2); (6) QC/QC composites derived from (3).

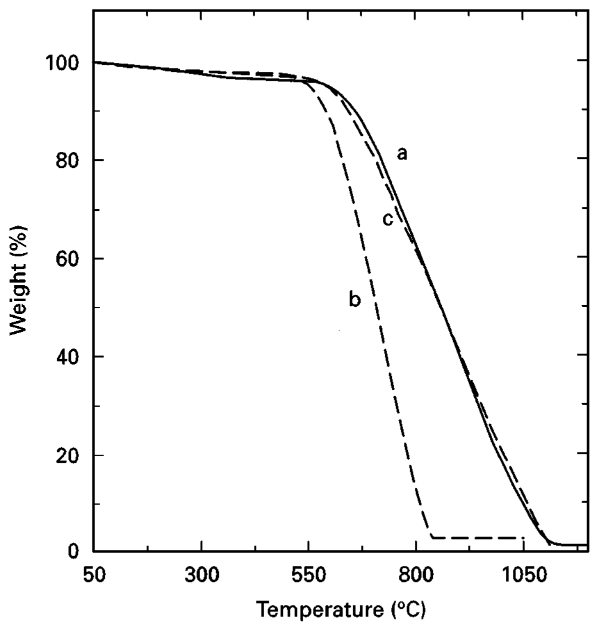


Figure 6 Dynamic TGA scans of QC/QC composites derived from three different precursors: (a) QFC-500/phenolic; (b) QFC-500/PAN; (c) OXPAN fibre/phenolic.

TABLE III Structural parameters of QC/QC composites derived from various precursors

QC/QC composites derived from	2θ (degree)	Half-width, B (degree)	Stack size, L_c (nm)
(a) QCF-500/phenolic	25.3	13.2	0.686
(b) QCF-500/PAN	25.6	8.2	1.104
(c) OXPAN fibre/phenolic	25.4	13.3	0.68

matrix. There is not much structural difference between QC/QC composites derived from QC fibre/phenolic and OXPAN fibre/phenolic precursors, as seen in Table III. Furthermore, because of low crystallinity (essentially no crystallinity for the phenolic resin) and lack of the high molecular orientation in both matrix resins, one would expect that the QC matrix also possessed a lower degree of crystallinity, and the structure of QC matrix was more imperfect than that of QC fibres even though they were pyrolysed at the same HTT of 500 °C. Thus, QC/QC composites had the low L_c value compared to the fibre components, as seen in Table I. A summary for the structural parameters of QC/QC composites can be found in Table III.

3.3. Oxidation behaviour

Results from the dynamic TGA scan in the air atmosphere for three various QC/QC composites are illustrated in Fig. 6. It was demonstrated that both phenolic matrix-derived QC/QC composites (a and c) had similar thermal stability with an onset decomposition temperature around 650 °C. The lower onset decomposition temperature around 530 °C for the PAN matrix-derived QC/QC composite (b) was because of the lack of three-dimensional network structure in the QC matrix, despite the fact that the composite exhibited relatively large L_c value. Therefore, phenolic matrix composite precursors would produce the QC/QC composites with better oxidation resistance than would the PAN matrix precursor.

Further thermal analysis data of QC/QC composites were obtainable by conducting the isothermal scan at the temperature range of 450 ~ 550 °C. Direct isothermal scan results and ln r versus $1/T$ plots at different burn-off (BO) stages for three QC/QC composites are shown in Figs 7–9, respectively. By comparison, it can be seen that the oxidation behaviour for the phenolic-derived QC/QC composites was characterized by an initial self acceleration (i.e. the oxidation rate (r) increases with the increase of the BO percentage or the weight loss percentage) at a BO stage up to 25% (Figs 7 and 9), after which the oxidation process occurred with the decreasing rate. The self-acceleration effect has been observed in many densified carbon materials such as conventional carbon fibres and C/C composites [12–14]. In order to explain the current observation, one has to consider the microstructure deviation of the QC/QC composites during the oxidation. As mentioned earlier, the phenolic-derived QC/QC composites had a compact structure which could make the initial oxidation difficult because of the lack of the active surface area (ASA). An increased BO value implied that the oxidation gradually broke off the extended two- or three-dimensional structure to form smaller carbon-based species, thereby increasing the ASA of the material. Therefore, the self-catalysis could be an initial characteristic of the oxidation in this type of QC/QC composites. At a BO of 25%, the materials were labelled as having larger ASA value with smaller structural species and more flaws among the turbostratic carbon ladders. Hence, after this stage, the oxidation was

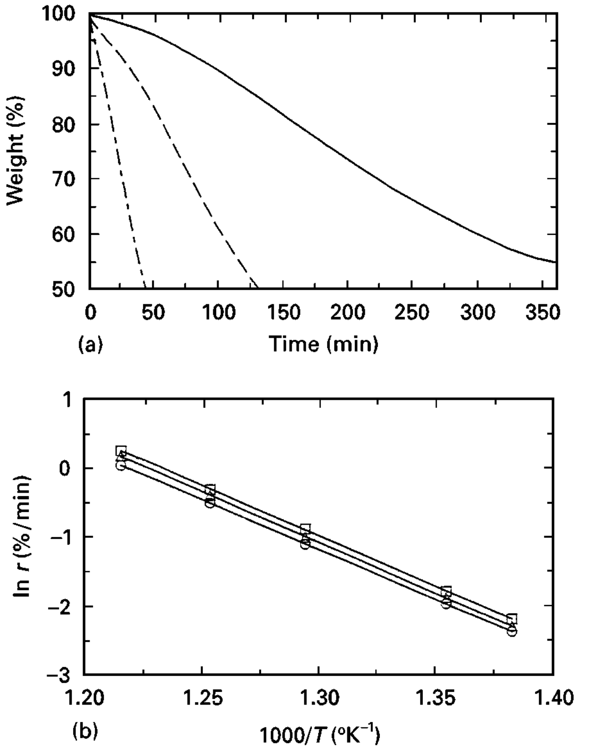


Figure 7 Isothermal scan results for QC/QC composite derived from QC fibre/phenolic composite precursor: (a) the weight loss percentage as a function of the oxidation time ((—) 450 °C; (– –) 500 °C; (- - -) 550 °C); (b) the variation of the oxidation rate (ln *r*) with $1/T$ at three different BO stages (○) 10% BO; (□) 25% BO; (△) 50% BO 550 °C.

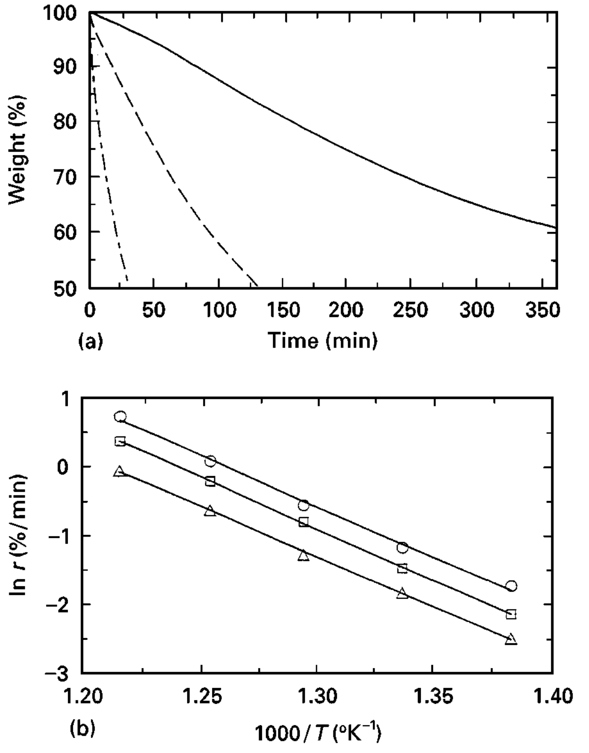


Figure 8 Isothermal scan results for QC/QC composite derived from QC fibre/PAN composite precursor: (a) the weight loss percentage as a function of the oxidation time; (b) the variation of the oxidation rate (ln *r*) with $1/T$ at three different BO stages. See Fig. 7 caption for key.

proceeding with a gradual annihilation of these small species, resulting in a decreasing oxidation rate.

In contrast, the oxidation process of the QC/QC composite derived from the PAN matrix precursor (b) in the overall measured BO range (0–50%) was characterized by the decreasing oxidation rate with the increase of BO value (Fig. 8). This behaviour can be attributed to the fact that this QC/QC composite exhibited an initial high ASA because of a variety of flaws existing in the turbostratic carbon structure which made the oxidation easy to occur initially. Thereafter, the situation was similar to that observed in the phenolic-derived QC/QC composite with a BO value above 25%. Thus, phenolic and PAN matrix derived QC/QC composites could follow the different oxidation mechanism even though they experienced a similar heat-treatment history.

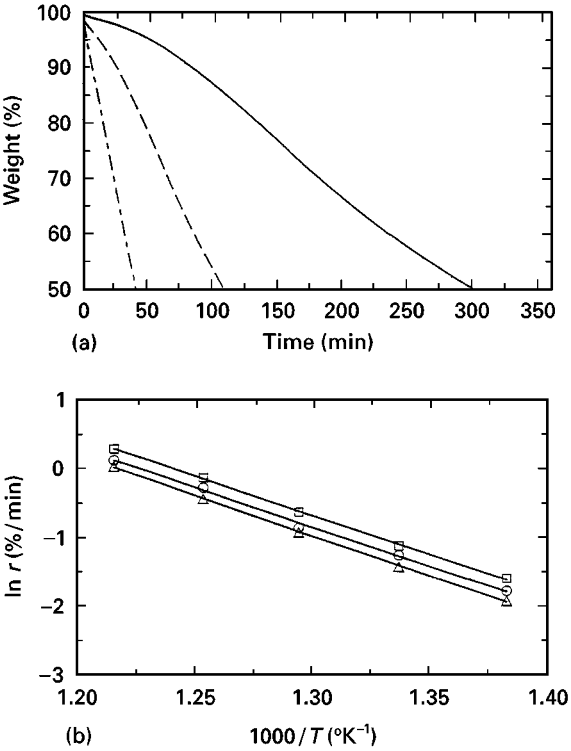


Figure 9 Isothermal scan results for QC/QC composite derived from OXPAN fibre/phenolic composite precursor: (a) the weight loss percentage as a function of the oxidation time; (b) the variation of the oxidation rate (ln *r*) with $1/T$ at three different BO stages. See Fig. 7 caption for key.

By applying the Arrhenius equation, both the activation energy for (Q) and pre-exponential constant (r_0) for the oxidation can be calculated; these have been summarized in Table IV. The fact that the QC/QC composite obtained from (a) exhibited a higher activation energy (125.8 kJ mol^{-1}) and a lower r_0 value than that derived from (b) indicated that the former possessed the higher oxidation resistance. The QC/QC composite from (c) showed the lowest Q value (96.5 kJ mol^{-1}), implying that strong chemical reactions between the fibre and the matrix during pyrolysis produced a considerable amount of defects which were less oxidation-resistant. But the low r_0 value possibly resulted from the more homogeneous nature of the fibre/matrix interface (Fig. 4). Thus, both low Q and r_0 values made the overall oxidation resistance comparable with that of the QC/QC composite derived from precursor (a). The conclusion is consistent with that obtained from the dynamic thermal scan.

TABLE IV The calculated oxidation constants from isothermal scans for QC/QC composites

QC/QC composites derived from	Activation energy, Q (kJ mol^{-1})	Pre-exponential constants, r_0 (%/min) $\times 10^7$		
		at BO 10%	at BO 25%	at BO 50%
(a) QC fibre/phenolic	125.8	10.61	13.22	11.73
(b) QC fibre/PAN	124.2	14.76	10.99	7.48
(c) OXPAN fibre/phenolic	96.45	0.156	0.181	0.132

3.4. Electrical properties

The main results on the electrical properties of composites are summarized in Table V. Because of the semiconducting nature of the fibre reinforcement, both QC fibre-reinforced phenolic and PAN matrix composite showed semiconducting characteristics with a positive E_a value. Meanwhile, because of both the fibres and the matrix being insulating, the electrical conductivity of the OXPAN/phenolic composite precursor was still in the insulating range. Again, the lower resistivity (ρ) and E_a values for the QC fibre/phenolic composite resulted from the more compact three-dimensional network structure of the matrix which held the semiconducting fibres together, forming more effective conducting path. After the partial carbonization, all QC/QC composites showed the decreasing resistivity and E_a value in comparison with their precursors. The smaller values in QC/QC composites derived from (a) and (b) precursors indicated that the large aromatic, sheet-like carbon structure may extend the mean free path of electrons, thus increasing the electrical activity. Fig. 10 illustrates a representative pyroresistance effect (log R versus $1/T$ plot) with a negative temperature coefficient for the QC/QC composite derived from the precursor (a). The result verified that the QC/QC composite was a semiconductor.

A unique electrical property has been also observed in the QC/QC composites as shown in Fig. 11. The non-linear I–V characteristic or the switching behaviour under the influence of an electrical field of about $10^2 \sim 10^3$ V cm^{-1} was similar to that observed in the semiconducting carbon fibres which were heat treated at a temperature range of 500–700 °C [10, 11, 15]. With the application of a voltage of up to 50 V corresponding to an electrical strength of about 500 V cm^{-1}, the material obeyed Ohm's law, exhibiting a line I–V response with a resistance of about 50 kΩ or the resistivity of about 10^4 Ω cm. The material was in a high resistance state or OFF state. After that, the curve approximately followed a relation of $I \propto V^2$ and gradually became exponential. As the voltage continued to increase, reaching a critical

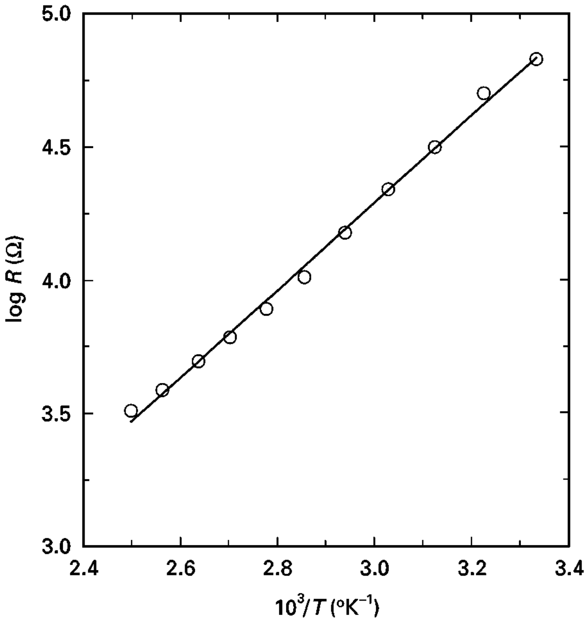


Figure 10 The representative pyro-resistance effect in the QC/QC composite.

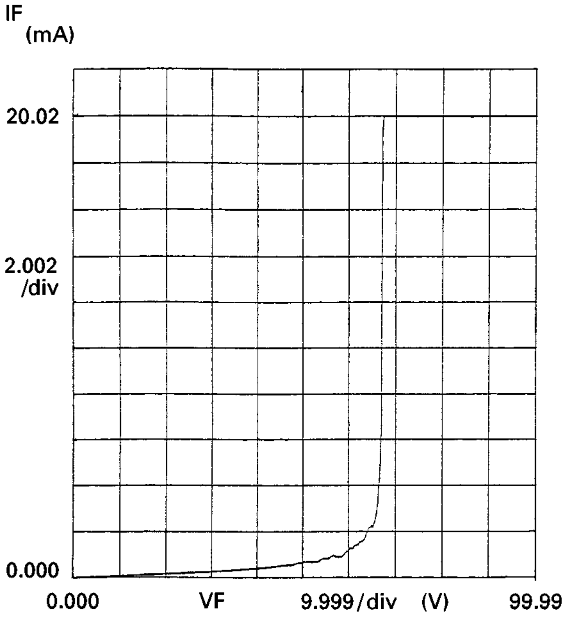


Figure 11 The non-linear I–V response for a QC/QC composite.

TABLE V Main electrical properties of QC/QC composites in comparison to those of their precursors

Composites	Resistivity, log ρ (Ω cm) at 25 °C	Activation energy, E_a (eV)
(a) QCF-500/phenolic	4.582	0.432
(b) QCF-500/PAN	5.027	0.521
(c) OXPAN fibre/phenolic	> 10	–
QC/QC-500 composites derived from		
(a)	3.432	0.325
(b)	3.971	0.403
(c)	5.011	0.508

threshold value of about 66 V, the current rose dramatically, possibly as high as 500 mA (because of equipment limitation, a current higher than 20 mA was not recorded). A 2 ~ 4 orders of magnitude decrease in resistivity of the sample has been observed. The material was thus excited to a low resistance state or ON state. During switching, the dynamic resistance (dV/dI) was estimated to be as low as 10–100 Ω. The interesting fact was that the complete withdrawal of voltage would bring the material back to the original OFF state. The transformation between the ON and the OFF states in these samples was completely reversible and reproducible depending upon the voltage applied. All three various QC/QC composite samples exhibited a similar switching behaviour except that the threshold voltage may vary because of different resistivity of materials. The observed behaviour in the semiconducting QC/QC composites could be very useful in the design of electronic switching devices.

3.5. Mechanical properties and failure mechanisms

The flexural stress–displacement diagrams of QC/QC composites and their precursors are shown in Fig. 12. The QC fibre/phenolic precursor had the maximum modulus and strength values with a step-wise fracture mode. In contrast, the OXPAN/phenolic precursor showed the lowest modulus and strength values with a brittle fracture mechanism. The flexural properties of the QC fibre/PAN composite were found between these two extremes. These observations could be closely related to the structure and properties of the fibres and the matrix, and the interface between the fibres and the matrix. Because of the cross-linking three-dimensional network structure, the mechanical properties of the phenolic matrix composite should be superior to those of its PAN matrix counterpart. The OXPAN fibres exhibited a lower modulus and a higher strength than the QC fibres which were heat treated at 500 °C (Table I). However, the OXPAN fibre/phenolic composite had both lower flexural modulus and strength than the QC fibres/phenolic composite. This phenomenon is possibly caused by the interface property of the composite. The OXPAN fibres may have less compatible physical wetting to the phenolic matrix, which leads to a low strength value.

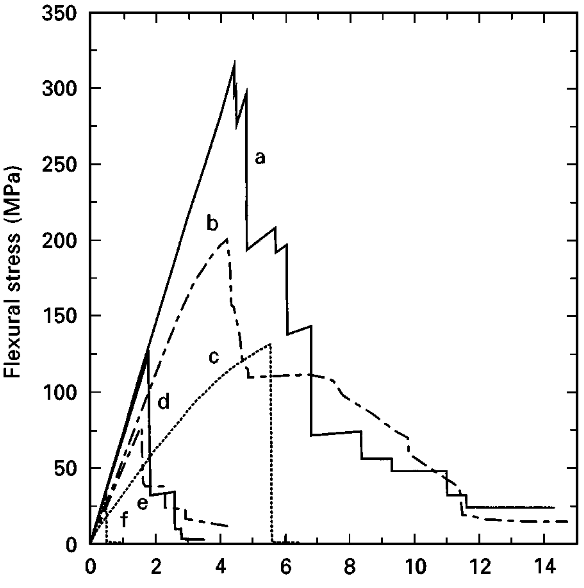


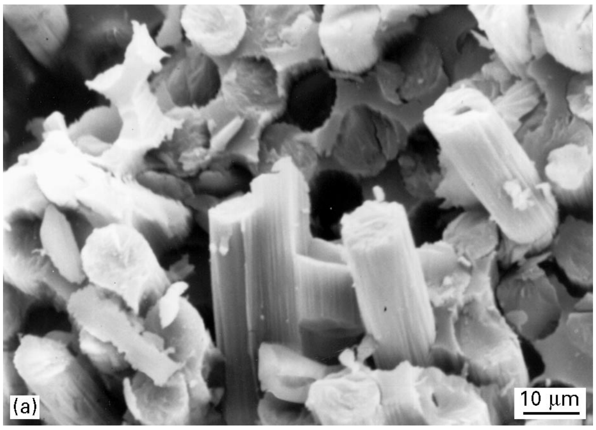
Figure 12 Flexural stress–displacement curves of QC/QC composites and their precursors. (a) QFC-500 phenolic; (b) QFC-500/PAN; (c) OXPAN fibre/phenolic; (d) QC/QC derived from (a); (e) QC/QC derived from (b); (f) QC/QC derived from (c).

TABLE VI A comparison in flexural strength and modulus between QC/QC composites and their precursors

Composites	Strength (MPa)	Modulus (GPa)
(a) QCF-500/phenolic	314.0	16.5
(b) QCF-500/PAN	201.1	8.38
(c) OXPAN fibre/phenolic	132.4	4.01
QC/QC-500 composites derived from		
(a)	124.3	22.4
(b)	78.5	11.3
(c)	30.2	7.67

Flexural test results for both QC/QC composites and their precursors are summarized in Table VI. It can be seen that after the partial carbonization, all QC/QC composites exhibited an increased modulus and a decreased strength in comparison with their precursors. The QC/QC composites derived from QC fibre-reinforced composite precursors showed better mechanical properties than those derived from OXPAN fibre-reinforced composite precursors because of less chemical interactions between the fibres and the matrix involved in the pyrolysis process, thus less deterioration of the QC fibres. The pyrolysis process to produce the QC/QC composite using the OXPAN fibre/PAN composite as precursor actually failed because of strong chemical reactions which completely damaged the fibre component. The resulting QC/QC composite exhibited extremely low mechanical properties. Both flexural strength and modulus of the QC/QC composite derived from the OXPAN fibre/phenolic composite precursor were yet at low levels, although they were better than those observed in a QC/QC composite with a similar pyrolysis process as studied by Ko *et al.* [6]. Therefore, strong chemical reactions in the process could make the QC/QC composite with a large amount of defects which are responsible for the observed low mechanical properties. Hence, the fact indicated that the composite containing the QC fibres as the QC/QC composite precursor had an advantage over that with the OXPAN fibre in achieving good quality of QC/QC composites. By comparison, it was also conclusive that the phenolic matrix-derived QC/QC composite had better mechanical properties than these PAN matrix-derived QC/QC composites.

Fig. 13 illustrates SEM observations on the fracture surface of the QC fibre/phenolic precursor and its QC/QC composite. The analysis indicated that the QC/QC composite and its precursor followed



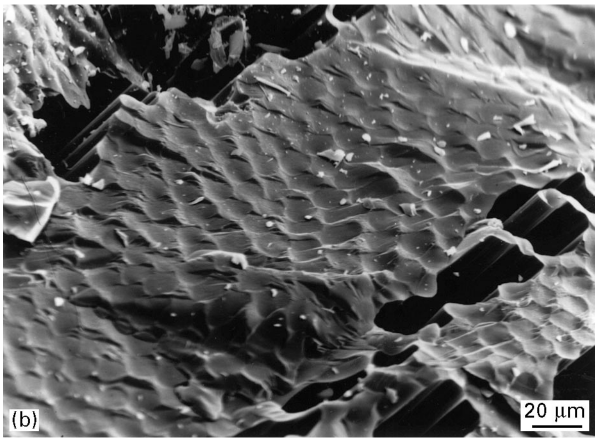


Figure 13 SEM photographs of the fracture surface: (a) the QC fibre/phenolic composite precursor (×1100) and (b) the QC/QC composite derived from the QC fibre/phenolic precursor (×400).

different failure mechanisms. The relatively ductile behaviour in the composite precursor was accompanied with either the fibre pull-out or delamination mechanism, which was consistent with the step-wise fracture mode observed in Fig. 12. As seen in Fig. 13a, the fracture mechanism of the QC fibre/phenolic precursor was actually fibre pull-out dominated. In contrast, because of the more homogeneous nature of the fibres and QC matrix, the QC/QC composite exhibited a catastrophic failure mode with a smooth fracture surface as demonstrated in Fig. 13b.

4. Conclusions

1. QC/QC composites derived from QC fibre- or OXPAN fibre-reinforced phenolic or PAN matrix composite precursors with similar processing history have shown different microstructure and thermal, electrical and mechanical properties.

2. TGA studies have revealed that the phenolic matrix-derived QC/QC had better thermal stability and oxidation resistance than the PAN matrix-derived QC/QC composites.

3. All QC/QC composites exhibited an increased flexural modulus and a decreased flexural strength compared to their precursors. QC/QC composites obtained from QCF reinforced composite precursors had better mechanical properties than those from OXPAN fibre reinforced composite precursors. The phenolic matrix derived QC/QC composites had better mechanical properties than the PAN matrix derived QC/QC composites.

4. The electrical resistivity of QC/QC composites lay within a semiconducting range. Unique switching behaviour has been observed in these materials. Their semiconducting nature combined with good mechanical and thermal properties would make these composite materials useful for electronic device applications.

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