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Bending fracture and acoustic emission studies on carbon–carbon composites: effect of sizing treatment on carbon fibres

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A comparative study using mechanical flexural tests and acoustic emission was carried out to determine the effect of carbon fibres with and without sizing treatment in carbon–carbon composites during the carbonization process. The composites had been fabricated in the form of two-directional polyacrylonitrile based carbon fibres impregnated with phenolic resin. It was found that the composites made with unsized polymer fibres result in better mechanical properties. Also the data obtained from acoustic emission appeared to show that the composites made with unsized fibres were more ductile. These results may be the result of the degree of adhesion at the interface between the fibre and the matrix. The bulk density and apparent porosity were measured as functions of the number of densification cycles and the results were correlated with the mechanical test results.

1. Introduction

Carbon-fibre-reinforced carbon matrix composites, or simply carbon–carbon (C–C) composites, are extremely-high-temperature materials which maintain their mechanical properties up to 3700 K in inert environments and up to 2000 K in oxidizing environments. These composites are commonly made using high-performance carbon fibres and thermosetting resins, such as phenol and furan derivatives, as precursors for the carbon matrix. In real applications, a study of the mechanical properties of C–C composites is one of the primary concerns for the prediction of composite behaviours [1], together with a study of oxidation reaction inhibition for the prediction of the working life of C–C composites in oxidizing environments [2].

It is generally accepted that good mechanical properties and long durability of the composites depend largely on the fibre–matrix interfacial adhesion in the case of carbon-fibre-reinforced plastic matrix composites [3], since the load stress transferred from the matrix to the fibre would require strong adhesion at the interfaces of the constitutive elements rather than a high cohesive density. Strong adhesion is commonly achieved by either oxidation or non-oxidative surface pre-treatments of the carbon fibres which may result in increasing the surface (or interface) energy characteristics, i.e., surface free energy, active functional groups and energetically different crystallite faces [4–6]. Moreover, it is known that a sizing treatment of fibre surfaces plays an important role in the anti-isotropic shrinkage of the matrix during the carbonization process, and it finally leads to high-performance composites. Our present focus is from the viewpoint of the physicochemically preferential bonding characteristics of the solid surface, since the fibre surface potential in the sizing process appears to be weak, exhibiting polymer properties [7, 8]. Also thermal isotropic shrinkage is considered to occur by chemical decomposition to the resin matrix, rather than by slight physical interaction, i.e., van der Waals attractions and hydrogen bonding mechanisms, of the fibre–matrix [9].

The object of the present study is to provide understanding of the effects of polymer sizing treatment on the strength behaviour of C–C composites. The roles of thermal volume change, apparent porosity and bulk density during the carbonization process and mechanical flexural behaviour as functions of the number of densification cycles of impregnation–carbonization of both C–C composites are discussed.

Meanwhile, it is well known that easily recognizable sources of acoustic emission (AE) in fibre-reinforced composites are matrix cracking, fibre–matrix interface debonding, fibre fracture and delamination [10]. During the mechanical flexural tests on both C–C composites, the AE was monitored as a function of load. The data recorded were analysed and also discussed, together with the results obtained from the mechanical techniques.

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2. Experimental procedure

2.1. Sample preparation: thermomechanical tests

Polyacrylonitrile based high-strength carbon fibres (Toray T-300, 6000 monofilaments) with and without sizing treatment were used in the form of plain weave made from fibres which were treated through commercial standard oxidation. The resol type of phenolic resin was used as the matrix precursor of the C–C composites to be studied.

The green composites made of eight plies of resin-impregnated carbon fabrics were prepared in an autoclave at 1.0 MPa and 490 K for 60 min. The thermomechanical properties were characterized from thermal thickness changes or thermal expansion of the specimens using a Du Pont Co. model 9900 thermomechanical analyser up to 970 K.

The apparent porosity and bulk density of the composites characterized by the water displacement technique [11] were investigated at room temperature as functions of heat treatment temperature (HTT) up to a maximum of 1370 K.

The resin-impregnated carbon fabrics were densified by liquid-phase impregnation and pyrolysis [12] and were carbonized up to 1370 K in an inert atmosphere. The heating rate to the carbonization temperature was fixed at 2 K min^{-1}. The retention time of the specimens at 1370 K was 128 min.

Five subsequent densification cycles consisting of impregnation of phenolic resin and carbonization were performed in order to decrease the apparent porosity of the composites. The experimental conditions were always the same as those for the green composites. The specimens were cut from the panels using a water jet; the dimensions were about 60 mm long, 2.5 mm thick and 10 mm wide.

2.2. Mechanical flexural tests

The composites were then characterized by three-point bending tests as mechanical flexural tests (the distance between supports divided by the thickness of specimen, $L/d = 16$; cross-head speed, 1.0 mm min^{-1}). The bulk fibre volume fraction of the green composites was about 60% (± 2%) for all composites, and more than seven specimens were tested for each of the C–C composites.

2.3. Acoustic emission procedure

Fig. 1 shows the schematic diagram of AE detection during the mechanical flexural tests. The acoustic signal was detected by a piezoelectric transducer which converts it into an electrical signal. This signal was amplified in order to obtain reliable AE data as a function of time. Three types of data were collected: event counts, cumulative event counts and relative signal energy distribution derived from the peak amplitude of the AE responses. These AE signal types have been used to identify the source of composite damage. The AET model MAC300L transducer with a resonant frequency of 300 kHz was located in the test section. Silicone grease was used as a couplant at the interface and the sensor was held in place with adhesive tape. The transducer was connected to a 60 dB, 250–500 kHz AET model 160B bandpass filter and preamplifier which fed the signal to an AET model 5000 AE analyser. The total amplification of the recording system was 86 dB with a threshold of 0.5 V.

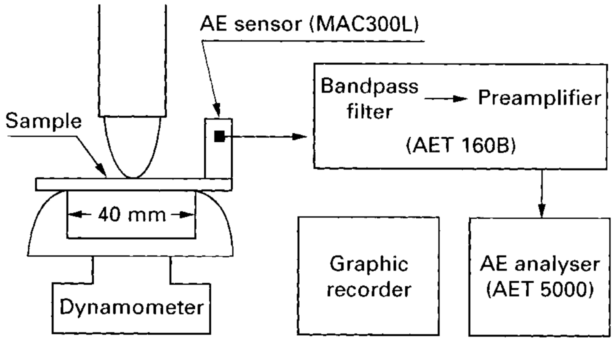

Figure 1 Schematic apparatus of AE detection during the mechanical flexural tests.

3. Results and discussion

3.1. Thermal behaviour of C–C composites

In the two-directional C–C composite carbonization process at temperatures up to 1370 K, the apparent porosity and bulk density of C–C composites as functions of HTT for carbon fibres without and with sizing treatment are shown in Figs 2 and 3, respectively.

As expected, the bulk density increases as the apparent porosity decreases. The behaviours of both C–C composites studied suddenly change in the HTT range 670–870 K, which may be shown to be a result of the volume change of the degrading matrix. The thermomechanical analysis (TMA) technique was applied to determine the thermal thickness change or thermal expansion of the specimens. The TMA results, given in Fig. 4, show that the specimen dimension of the C–C composites decreases rapidly at about 770 K. This is explained by the high isotropic shrinkage of the resin matrix which causes voids, pyrolysis cracks and, in the worst case, delamination.

According to the results of the cured phenolic resin investigated by Lum *et al.* [13], the outgassing of free

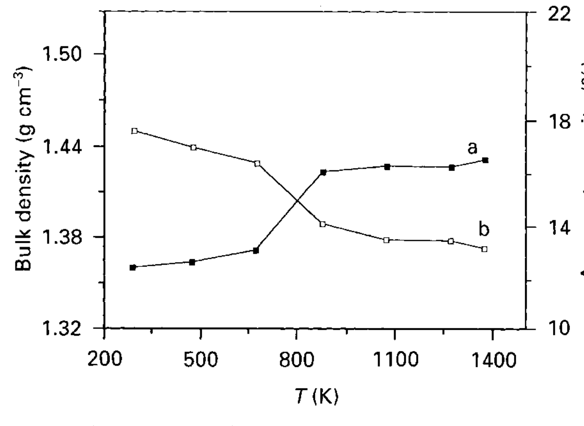

Figure 2 Apparent porosity (curve a) and bulk density (curve b) of C–C composites as functions of HTT for carbon fibres without sizing treatment.

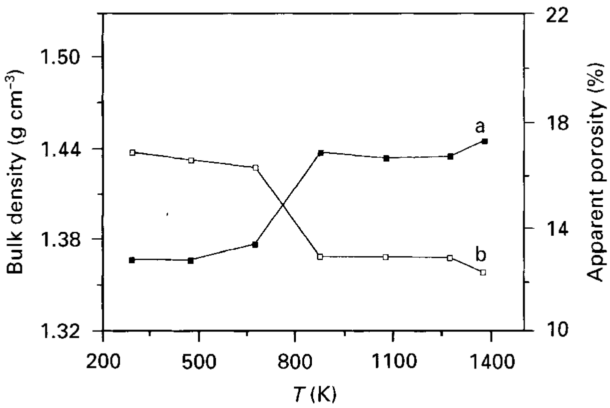

Figure 3 Apparent porosity (curve a) and bulk density (curve b) of C–C composites as functions of HTT for carbon fibres with sizing treatment.

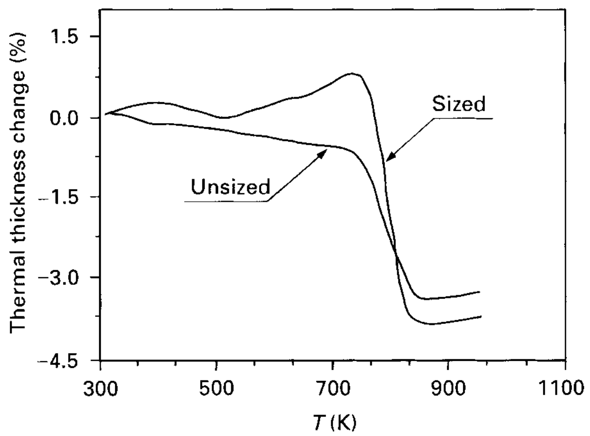

Figure 4 TMA diagram of the C–C composites for unsized and sized carbon fibres.

phenol and the formation of water, CO and CO_2 takes place at a low temperature (below 620 K), and low-weight molecular compounds such as aromatic species are released by thermal fragmentation of the polymer structure between 620 and 770 K. It is noted that the behaviours of all C–C composites studied are similar to those of the cured phenolic resin. As a consequence, the isotropic shrinkage largely depends on the resin matrix property changes due to thermal decomposition during the carbonization process. Also the isotropic shrinkage of the matrix results in the outgassing of very-low-weight aromatic species at about 770 K. Here it demonstrates that more precise and detailed thermal behaviour of the composites should be determined to explain the sudden changes in the open pore volumes in the resin matrix at the HTT of 670–870 K for the high-performance composites.

As shown in Fig. 4, relatively less thermal expansion, which may show local and transient composite defects (or delamination) during the carbonization process is observed in the C–C composites made from unsized carbon fibres. This result may explain why the outgassing of polymer sizing agents, e.g., commercial epoxy resin, appears to form the open pore volumes in composites. Consequently, it can cause damage to the composites. In other words, the fibre sizing treatment using low-surface-characteristic polymer agents may result in a decrease in the degree of adhesion at the interface between the fibre and the resin matrix.

3.2. Mechanical properties of C–C composites

For a rectangular cross-section of the composites, the flexural strength, σ_f, and the elastic modulus, E_b, in flexure were studied as functions of the number of densifications. σ_f and E_b for the composites determined from three-point bending tests are calculated using the following equations [14]:

$$\sigma_f = \frac{3}{2}\frac{PL}{bd^2} \tag{1}$$

$$E_b = \frac{L^3}{4bd^3}\frac{\Delta P}{\Delta m} \tag{2}$$

where P (N) is the applied fracture force, L (m) the distance between the supports, b (m) the width of the specimen, d (m) the thickness of the specimen, ΔP (N) the change in fracture force in the linear portion of the load–deflection curve and Δm (m) the change in deflection corresponding to ΔP.

Figs 5 and 6 show the flexural strength and the elastic modulus in flexure of the C–C composites, respectively, as functions of the number of densifications. These results indicate that, as the number of densifications increases, the composites made with unsized carbon fibres have relatively higher mechanical properties than do the composites made with sized carbon fibres.

As seen in Fig. 7, the bulk density increases and the apparent porosity decreases as the number of densification cycles in both C–C composites increases; also the bulk densities of the composites made with unsized fibres are higher than those of the composites made with fibres that were sized. It is considered that increasing the bulk density is of paramount importance in improving the mechanical properties of C–C composites. Also it clearly reveals that the sizing treatment is not effective from the viewpoint of improving the flexural properties of the two-directional carbonized

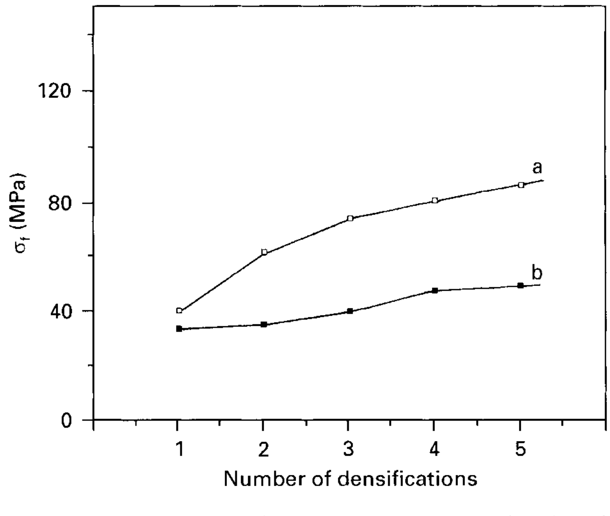

Figure 5 Flexural strength of the C–C composites as a function of the number of densifications. Curve a, unsized; curve b, sized.

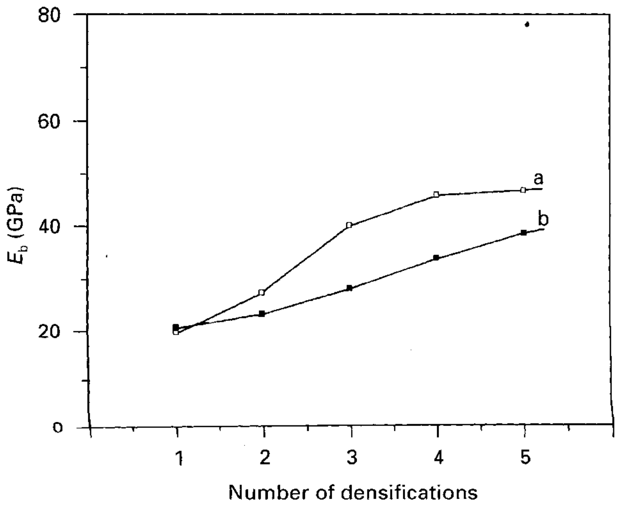

Figure 6 Elastic modulus in flexure of the C–C composites as a function of the number of densifications. Curve a, unsized, curve b, sized.

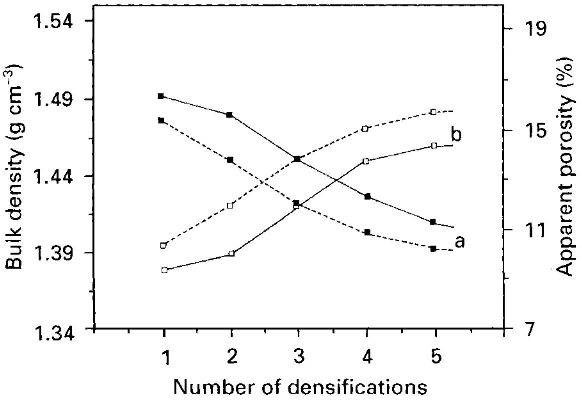

Figure 7 Apparent porosity (curves a) and bulk density (curves b) of C–C composites as functions of the number of densifications for unsized (---) and sized (—) carbon fibres.

composites. This seems to be a consequence of the weakening of fibre–matrix physical adhesion of the C–C composites studied.

3.3. Acoustic emission analysis

Fig. 8 shows the AE event counts of both C–C composites studied as a function of the time up to 60 s during the mechanical flexural tests. It shows that the event counts of both C–C composites made from carbon fibres with and without sizing treatment were recorded throughout all the elapsed time range and increased between 0 and 15 s and between 0 and 20 s, respectively. The results on the retarded time of maximum event counts, in the case of the composite property changes, include the physicochemically improved degree of adhesion at the interface between the fibre and the matrix. Similar results obtained from the cumulative AE event counts of both C–C composites studied versus elapsed time demonstrate that the composites made with unsized carbon fibres have relatively fewer cumulative event counts than do composites made with sized carbon fibres, as shown in Fig. 9. The AE responses for the composites made with sized fibres may possibly be explained as arising because the sizing treatment on fibre surfaces causes the composites to have intrinsic brittle properties.

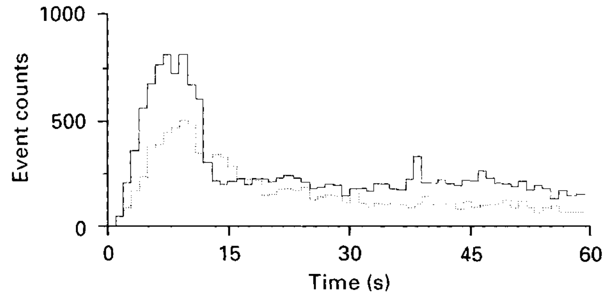

Figure 8 A comparison of AE event counts of both green C–C composites as a function of elapsed time. (·····), unsized; (—), sized.

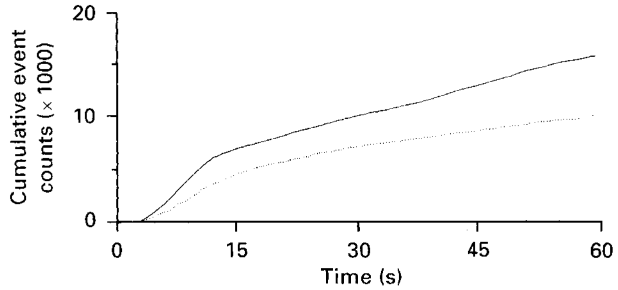

Figure 9 A comparison of cumulative AE event counts of both green C–C composites as a function of elasped time. (·····), unsized; (—), sized.

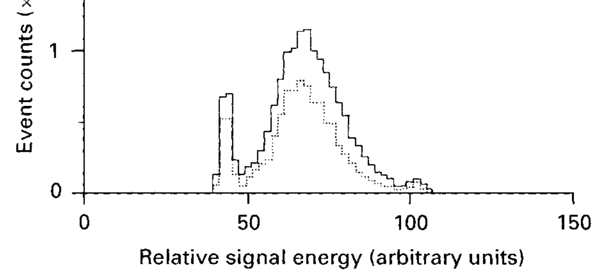

Figure 10 A comparison of AE event counts of both green C–C composites as a function of relative signal energy during the elapsed time of 60 s. (·····), unsized; (—), sized.

It is generally accepted that the increased emission event counts are due to composite damage and that the event counts with low, middle and high range responses are generated from matrix cracking, debonding at the fibre–matrix interface, and fibre relaxation and fracture during composite fracture, respectively [15, 16]. As shown in Fig. 10, the AE event responses as a function of relative signal energy, during the elapsed time, clearly demonstrate three sections. Therefore it is considered that the damage of two-directional C–C composites is largely dominated by fibre–matrix interface debonding during composite fracture. Also a decrease in AE event counts with increase in the relative signal energy may be observed for the composites made from unsized carbon fibres. As mentioned above, this is due to the increase in the ductile interface properties or to the increase in the degree of fibre–matrix adhesion in the case of composites with unsized fibres.

4. Conclusion

From the results of bending fracture and AE studies, the presence of commercial sizing agents of reinforced carbon fibres during the carbonization process produces degradation in two-directional composites. In particular the results obtained from TMA show that less thermal expansion is observed in the composites made from unsized carbon fibres. It seems that the polymer sizing agents outgas during carbonization and accordingly they influence the composites.

As observed from AE studies, the major damage to the composites is dominated by debonding at the fibre–matrix interface rather than by matrix cracking and fibre relaxation and fracture during composite rupture. It is thus considered that an effective and optimized surface treatment of reinforced fibres may be necessary to improve the degree of adhesion or ductile properties at the fibre–matrix interface for high-performance two-directional C–C composites.

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