The carbon black effect on crack formation during pyrolysis step in liquid silicon infiltration process for Cf/C-SiC composites

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The formation of crack patterns during the pyrolysis step, which converts the carbon fiber-reinforced plastic composite (CFRP) to a Cf/C composite as one step in the liquid silicon infiltration (LSI) process, was investigated. Generally, cracks occur as a result of variances in thermal shrinkage between the matrix and the fiber during pyrolysis. The addition of carbon black powder as a filler resulted in a reduction in the shrinkage, but more cracks were formed. The transversal crack increased, and the partial delamination was newly occurred as the filler was increased. The properties of the matrices also changed; the fracture toughness decreased, and the void area increased. Consequently, the crack formation occurs not only by the thermal shrinkage difference between fiber and matrix but also the effect of matrix fracture toughness or void content. The flexural strength of LSI-processed samples was also measured, and the filler improved the mechanical strength but reduced its reliability.

Key-words: Cf/C-SiC, Composite, Matrix, Infiltration, Crack, Pyrolysis

1. Introduction

Ceramic matrix composite (CMC) materials were developed for high-temperature applications, such as heat shields or thermal protection for spacecraft. Different processing techniques are currently in use for the manufacture of complex-shaped ceramic matrix composite components. A novel technology called liquid silicon infiltration (LSI) to produce CMC structures with lower costs and shorter manufacturing times has been developed at DLR (German Aerospace Center).

The LSI process is based on the infiltration of commercially manufactured carbon fiber/carbon with molten silicon and leads to so-called Cf/C-SiC materials.1) The LSI process consists of three steps: (1) fabrication of CFRP; (2) pyrolysis of CFRP to form a porous Cf/C; and (3) infiltration of molten silicon through cracks in Cf/C and the formation of a Cf/C-SiC composite.2) It is well known that the properties of CMCs are determined not only by the fibers and matrix themselves, but also mainly by the microstructure of the matrix.3) The fabrication of high-performance CMC requires an understanding of the rules governing LSI process.

During LSI, molten silicon is infiltrated through crack which is formed by variance in thermal shrinkage during the pyrolysis of fiber-reinforced polymer composite and forms α-SiC and β-SiC with free Si;4)–6) thus, the crack patterns of the matrix govern the final properties of composites. Although some efforts have been made to understand the pyrolysis, only few studies have attempted to elucidate the siliconization of carbon/carbon preforms.7)–9) J. Schulte-Fischbeck10) studied the development of the crack pattern and determined that it was affected by the shrinkage of the resin during thermal treatment. Bulau11) observed the development of cracks during pyrolysis using an acoustic emission method. He reported that the difference in the CTE of fibers and the matrix leads to the formation of cracks. These publications describe some important details of the pyrolysis that explain the general theory of the types of cracks and their interactions.

In this study, the filler effect on matrix cracking during pyrolysis was investigated based on the general crack development mechanism previously published. The carbon black powder was added as a filler material into phenol resin, and Cf/C-SiC was fabricated by LSI. The carbon black filler changes the shrinking properties of matrix and increase pyrolytic carbon yield after pyrolysis step. The crack formation was observed and evaluated as contents of carbon black filler.

2. Experimental procedure

2.1 Materials

The carbon fiber fabric was used as a reinforcement for the fabrication of Cf/C-SiC composite. The carbon fabric was 6K plain weave, and its filament diameter was 7μm (T-300, Toray, Japan). The phenol resin (KRD-HM2, Kolon Chemical, Korea) was used for the polymeric matrix as a composite, and carbon black powder (HIBLACK 30L, 24 nm, Korea Carbon Black Co., Ltd., Korea) was added to the phenol resin as a matrix filler.

2.2 Preparation of samples

The carbon black powder was added into phenol resin and mixed with a mechanical stirrer for 1 hour. The amounts of carbon black filler are listed, and each sample notation is shown in Table 1. These slurries were impregnated with carbon fiber fabric and stacked 20 plies. Under vacuum bagging, the 20-ply stacks were cured at 80°C for 24 h as recommended by the supplier and post-cured at 200°C for 10 hours. The cured samples were heat-treated for pyrolysis in a nitrogen atmosphere at 1000°C for 1 h, and the temperature ramp-up rate was 1°C/min. The LSI process was performed with a pyrolized preform at 1650°C in vacuum, and the Cf/C-SiC composites were finally obtained. Also, to evaluate the properties of each matrix, the slurries were cured without carbon fiber fabric and pyrolyzed using the same method.

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2.3 Measurement

The viscosity of phenol resin with a carbon black filler was determined by a viscosimeter (Brookfield LVDV-I+; Japan) with 20% rpm, and the density of cured matrices was measured using the Archimedes method. Generally, the cracks after pyrolysis are induced by thermal mismatch; thus, the shrinkage of matrices during pyrolysis is measured with a dilatometer DIL 402C (Netzsch, Germany) at the same temperature and atmospheric condition of LSI process. The microstructures were observed with SEM, and the crack area was evaluated with image analysis software (ImagePro Plus, Media Cybernetics, USA). The fracture toughness of the pyrolyzed bulk matrix without fiber was measured using a micro indentation technique with a micro indenter (Akashi HM-124, Japan) with 2 kgf for 10 sec., and the equation is expressed below.12,13)

\[ K_c = \frac{\varphi(E/H)^{1/2}}{P/C_d^{1/2}} \]

\((K_c: \text{fracture toughness, } \varphi: \text{material-independent constant, } E: \text{elastic modulus, } H: \text{hardness, } P: \text{load, } C_d: \text{crack dimension})\)

The mechanical properties were measured using a flexural strength test, and the Weibull modulus was evaluated for its reliability. The samples were fabricated after LSI at a dimension of \(3 \times 4 \times 50\) mm, and the test was performed according to standard ASTM C1161. For the Weibull modulus calculation, 25 samples were tested for each condition, and Equation was used for the calculation.14)

\[ P = 1 - \exp\left(-\frac{(\sigma_f/\sigma_0)^m}{m}\right) \]

\((\sigma_f: \text{inert strength, } \sigma_0: \text{scaling stress, } m: \text{Weibull modulus, } P: \text{Weibull failure probability})\)

3. Result and discussion

The viscosity of the slurry is shown in Table 1; as the carbon black content increased, the viscosity simultaneously increased. The viscosity of neat resin was under 500 cps, which easily permits infiltration; however, the CB-20 matrix shows 5800 cps, which is very difficult to use in an infiltration process. The densities of cured samples are also shown in Table 1. The density was increased with the carbon black content because the raw density of carbon black is higher than that of phenol resin.

Each cured matrix was pyrolyzed in nitrogen atmosphere, and the TGA result is shown in Fig. 1. The pyrolysis is divided into four stages on the basis of its chemistry: post-curing (~400°C), main pyrolysis (400–600°C), dehydrogenation (600–1200°C), and defect curing (1200°C ~).10,15,16) During main pyrolysis, the conversion of the phenol resin \(C_nH_{2n}OH\) is decomposed as \(C, H\), and \(H_2O\) so that there is no reaction between carbon black filler and phenol resin. After dehydrogenation, only carbon remained, and the carbon yield, shown in Fig. 1, increased with the carbon black filler content. The carbon yield was 62% of neat resin but increased to 72% when carbon black filler was added into the neat resin. These results could be correlated with the strain change during pyrolysis, as shown in Fig. 2. The strain rapidly decreased in the main stage of pyrolysis and stabilized during dehydrogenation. Finally, the shrinkage of neat resin was 20%, but only 16% strain was shrunk when 20% of carbon black filler was added into the neat resin. While the resin shrink largely during pyrolysis step, the carbon fiber shows very little thermal expansion or shrinkage in longitudinal direction. While resin shrinks considerably during pyrolysis, carbon fiber shows very little thermal expansion or shrinkage in a longitudinal direction. This difference in the thermochemical shrinkage between the matrix resin and the reinforcing fiber leads to the development of crack pattern.10)

It is easily predictable that, as the difference in shrinkage increases, more cracks appear; however, Figs. 3 and 4 demonstrate otherwise. Figures 3 and 4 show the cracking after pyrolysis of the carbon fabric laminate with each slurries of phenol and carbon black filler mixture. The density and the size of the cracks increased in proportion to the content of carbon black filler. Without the carbon black filler, the crack area was only 1.23%, but it increased up to 3.4% when 20% of the filler was added. Without the filler, most of the cracks that formed inside of the fiber bundle were transversal (in Fig. 3 denoted with ‘a’). However, transversal cracks and partial delamination (in Fig. 3 denoted with ‘b’) between bundles occurred when carbon black filler was added.10,17) These cracks occur as debonding of the fiber-matrix interface because the interface between the fiber and the matrix of CFRP and C/C composite material is the weakest link, as the fiber and the matrix are connected by an interaction of van-der-Waals force and chemical bonds in both.18)
Near the interface, since shrinking of the matrix is prevented by stiff fibers, a mixture of normal and shear stress occurs. This complex, three-dimensional stress leads to a reduction in the strength of the matrix. The microstructure also shows an increase of pores with the addition of a carbon black filler, and channels could be developed by these pores in the interface that act as initiation sites for debonding. The propagation and combination of transversal cracks deflected and interrupted between the warp and weft fibers where the partial delamination occurs. Consequently, the addition of the carbon black filler reduced the interfacial bonding strength between the fiber and the matrix, and this weakness induced a large amount of transversal cracking that propagated until partial delamination occurred during pyrolysis.

Bulk matrix samples were fabricated without reinforcing fiber to evaluate the mechanical properties of the matrix that had no cracking but voids inside, and the relative fracture toughness after pyrolysis was measured as shown in Fig. 5. The relative toughness of the bulk matrix decreased with an increase in the content of the carbon black filler. The void area in each bulk matrix is shown in Fig. 6, and it increased in proportion to the carbon filler content. Since the carbon black filler contains gases due to its agglomerated morphology before mixing with phenol resin, the void area increased with the filler content. Cracks also easily formed by entrapped pores in the matrix during pyrolysis because of the high internal partial pressure. As a function of the void content Young’s modulus, the modulus of rupture and fracture toughness could be regressed so that the fracture toughness of the filler-added matrix decreased. It is possible to decrease the thermal shrinkage of the matrix during the pyrolysis process by adding a carbon black filler into the matrix; however, the increase of the void area by the filler after pyrolysis leads to poor fracture toughness and accelerates crack formation.

LSI process was followed after pyrolysis, as shown in Figs. 7 and 8 shows the flexural strength. Molten silicon was infiltrated through the pre-formed cracks during pyrolysis, and the silicon and carbon reaction amount was influenced by the crack area. The reaction occurs from crack surface and unreacted silicon remains as residual free silicon that weaken the mechanical properties in elevated temperature over 1200°C. Since the room temperature strength of the C/SiC composite is proportional to the amount of reacted SiC, the strength increased with the filler content. In Fig. 8, the Weibull modulus is also presented; it rapidly decreased with the addition of filler. Large numbers of pores in the filler-added matrix was observed after the pyrolysis step, and their shapes were not only sharp that weaken the mechanical properties but also sphere that can be crack arresting site. After LSI, the pores were filled and reacted with silicon as shown in Fig. 7, and these second phases enlarge the uncertainty of the composite material.
It was found that crack development was influenced not only by the thermal shrinkage difference between the fiber and the matrix but also by the fracture toughness and the void in the pyrolyzed matrix. Although the thermal shrinkage of the matrix decreased with the addition of filler material from the 20 to 16% strain, the amount of cracking was not reduced. The crack area increased from 1.23 to 3.4% as a result of the filler material due to the decreased fracture toughness and increased amount of the void in the matrix. The flexural strength improved due to the increase of silicon and carbon reaction area with the addition of the carbon black filler; however, the reliability drastically decreased.

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4. Conclusion

Control of crack formation was studied by adding a carbon black filler during pyrolysis step of LSI process. A specific amount of carbon black powder was added to phenol resin and laminated. The thermal shrinkage of matrices was measured with a dilatometer. The crack patterns were analyzed by image analysis software, and the mechanical properties of the matrices and the final LSI processed composite were evaluated.

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