

EFFECT OF INORGANIC FILLER ON CARBON-CARBON COMPOSITES TO ENHANCE THEIR SURFACE FREE ENERGY AND ILSS

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Introduction

Carbon fiber-reinforced carbon matrix composites (carbon-carbon composites) are new emerging materials with potential applications as high-temperature structural materials for the space and aeronautic industry [1]. Many important applications of general composites require that they link fiber-matrix interface due to the interface is the composite's weak link. At the interface, where two vastly different materials meet, the physical and mechanical properties change abruptly. Furthermore, the two materials are held together only by secondary (i.e., noncovalent) interactions. The continuous net of chemical bonds that exists within the material on either side of the interface does not exist across the interface. The discontinuity in physical and mechanical properties, as well as the interruption in molecular connectivity, makes the interface in an easy locus of failure in the composite [2].

The objective of the present work is to provide an understanding of the effects of inorganic fillers on the fiber-matrix interface of the carbon-carbon composites, and consequently their properties describe two viewpoint: surface free energy by contact angle measurements, and interlaminar shear strength (ILSS) by short-beam test.

Experimental

Polyacrylonitrile (PAN) based high-strength carbon fibers (Taekwang Ind., TZ-307, 12K) were used in the filament fibers of which were no sizing and no surface treatments. The resole type of phenolic resin (Kangnam Chem. Co.) was used as the matrix precursors of carbon-carbon composites to be studied. The MoSi_2 powders ($<2 \mu\text{m}$, supplied from Aldrich Co.) were used as an inorganic filler after pulverization by freezer/mill (Spexcertiprep Co., spex6700) in reduce their particle size to about $0.4 \mu\text{m}$ for

increasing of the interfacial adhesion areas. The composites were systematically prepared with MoSi_2 powders of 0, 4, 12 and 20wt% on the basis of resin matrix. The green composites were prepared as vacuum bagging method, and the laminates were subjected to the carbonization process at 1100°C at a heating rate of $10^\circ\text{C}/\text{hr}$. Specifics of the manufacturing process are presented elsewhere [3].

Contact angles were measured using the sessile drop method on a Rame-Hart goniometer. Contact angle measurements were performed within 5s of contact for the evaluation of critical surface tension. For this work, surface tension for the wetting liquids are shown in Table I and were used for the evaluation of surface free energies of the composites. Interlaminar shear strength (ILSS, $L/d = 4$; cress-head speed, $1.0 \text{ mm}/\text{min}$) of the composites was characterized by the short-beam test for the degree of adhesion at interfaces.

Results and Discussion

The adsorption, wettability, adhesion and morphology of the component phases are greatly affected by the interfacial or surface free energies, which is important for evaluating the physical and mechanical properties of a composite. In the early 1960's, Fowkes [4] introduced the concept of surface free energy, γ , which can be resolved into a London dispersive component (superscript: L) and specific (or polar, SP) component:

$$\gamma = \gamma^L + \gamma^{SP} \quad (1)$$

Here, γ^L describes the London attraction of van der Waals force and γ^{SP} ascribes all other nondispersive component of physical interactions (Debye and Keesom contributions of van der Waals, H-bonding, and other small polar effects).

During equilibrium contact angle (abbreviated θ here) measurement for a liquid drop on ideally smooth and homogeneous solid surfaces, Owens and Wendt [5] and Wu [6] extended the Fowkes' concept using geometric mean, as follows:

$$\gamma_L (1 + \cos \theta) = 2(\gamma_L^L \cdot \gamma_S^L)^{1/2} + 2(\gamma_L^{SP} \cdot \gamma_S^{SP})^{1/2} \quad (2)$$

In more practical relationship based on two simultaneous liquids of widely different properties on solid surfaces, e.g., water and diiodomethane for largely polar and nonpolar liquids, respectively, γ_S^L and γ_S^{SP} can be solved:

$$\gamma_S^L = \frac{1}{4} \left[\frac{(1 + \cos \theta_1) \gamma_1 \cdot (\gamma_2^{SP})^{1/2} - (1 + \cos \theta_2) \gamma_2 \cdot (\gamma_1^{SP})^{1/2}}{(\gamma_1^L \cdot \gamma_2^{SP})^{1/2} - (\gamma_2^L \cdot \gamma_1^{SP})^{1/2}} \right]^2 \quad (3)$$

$$\gamma_S^{SP} = \frac{1}{4} \left[\frac{(1 + \cos \theta_2) \gamma_2 \cdot (\gamma_1^L)^{1/2} - (1 + \cos \theta_1) \gamma_1 \cdot (\gamma_2^L)^{1/2}}{(\gamma_1^L \cdot \gamma_2^{SP})^{1/2} - (\gamma_2^L \cdot \gamma_1^{SP})^{1/2}} \right]^2 \quad (4)$$

The results of interfacial tensions or surface free energies of the composites studied are shown in Fig. 1. The carbon-carbon composites made with 12wt% MoSi₂ gives maximum interfacial tension that is mainly due to its higher London dispersive component, γ_S^L .

The degree of adhesion at interfaces between fiber and matrix may be measured by the short-beam test for ILSS of the mechanical behaviors. The ILSS is calculated as follows:

$$ILSS = \frac{3F}{4bd} \quad (5)$$

where F (N) is the rupture force, b (m) the width of the specimen, d (m) the thickness of the specimen.

From the ILSS results as shown in Fig. 2, the presence and the increasing of the amount of MoSi₂ leads to the increase of ILSS of carbon-carbon composites. Also the increasing of ILSS is closely related to the growing of surface free energy of the composites, especially London dispersive component. From which, it can be resulted that the increase of MoSi₂ on the composites increases the adherent surface areas between fibers-matrix-inorganic fillers.

References

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Table 1. Surface tension (γ_L) and London dispersive (γ_L^L) and specific (γ_L^{SP}) components of wetting liquids

Wetting liquids	γ_L^L /mJ.m ⁻²	γ_L^{SP} /mJ.m ⁻²	γ_L /mJ.m ⁻²
Water	21.8	51.0	72.8
Diiodomethane	50.42	0.38	50.8

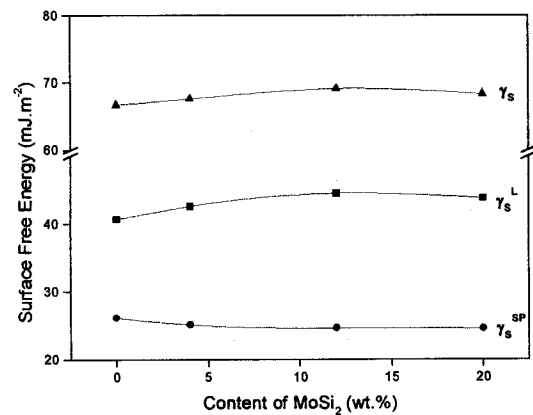


Figure 1. Surface free energies (in mJ.m⁻²) of carbon-carbon composites as content of MoSi₂ using a two-liquid geometric method.

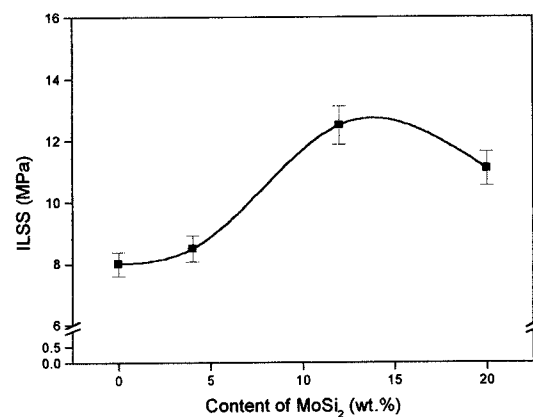


Figure 2. Interlaminar shear strength (ILSS) of carbon-carbon composites as content of MoSi₂.