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Effects of Fiber Surface-Treatment and Sizing on the Dynamic Mechanical and Interfacial Properties of Carbon/Nylon 6 Composites

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Abstract

The effects of fiber surface-treatment and sizing on the dynamic mechanical properties of unidirectional and 2-directional carbon fiber/nylon 6 composites by means of dynamic mechanical analysis have been investigated in the present study. The interlaminar shear strengths of 2-directional carbon/nylon 6 composites sized with various thermosetting and thermoplastic resins are also measured using a short-beam shear test method. The result suggests that different surface-treatment levels onto carbon fibers may influence the storage modulus and tan δ behavior of carbon/nylon 6 composites, reflecting somewhat change of the stiffness and the interfacial adhesion of the composites. Dynamic mechanical analysis and short-beam shear test results indicate that appropriate use of a sizing material upon carbon fiber composite processing may contribute to enhancing the interfacial and/or interlaminar properties of woven carbon fabric/nylon 6 composites, depending on their resin characteristics and processing temperature.

Keywords : *Carbon/nylon 6 composites, Dynamic mechanical property, Interfacial properties, Surface-treatment, Sizing*

1. Introduction

The interfacial and mechanical properties of a fiber-reinforced polymer composite are significantly influenced by interfacial characteristics between the reinforcing fibers and the polymer matrix [1-3]. Especially for carbon fibers, the surface is an important region that plays a contributing role in the interfacial behavior with the polymer matrix. Their interfacial characteristics can be chemically or physically altered by both fiber surface-treatment and sizing. Appropriate surface-treatment may modify the fiber surface by increasing the surface area and/or by increasing oxygen-containing functional groups on the surface that may provide some chemical interactions between the fibers and the matrix resin [4, 5].

Sizing may further increase the interfacial property with the interphase formation between the fiber and the matrix in a composite. Choosing a size for carbon fibers considerably depends on the polymer matrix resin. The compatibility of the size with the matrix resin may significantly influence the interfacial adhesion. A sizing interphase may be partially soluble with polymer matrix resin, resulting in some possible interdiffusion between them [6]. Also, both content and thickness of a size may affect the interfacial characteristics of a composite [7]. To optimize the sizing effect, appropriate sizing materials for carbon fibers should be applied according to the purpose and application of a composite to be used.

Dynamic mechanical properties, in terms of storage modulus, loss modulus and tan δ, have been studied to examine the interfacial characteristics of carbon fiber- or glass fiber-reinforced polymer composites [8-10]. The dynamic mechanical behavior of a composite material may be responsible for changes in the molecular mobility and the interfacial behavior between the fiber and the matrix. During measurement, a composite specimen is deformed exhibiting dynamic mechanical responses by a sinusoidally oscillating stress with temperature and frequency.

Composite laminate tests are often used to directly measure fiber-matrix adhesion in a fiber-reinforced polymer matrix composite. Short-beam shear test is useful for examining the interfacial properties between the fiber and the matrix in a woven fabric-reinforced polymer composite system, resulting in the interlaminar shear strength (ILSS) [11, 12]. This test is quite similar with a three-point bending test method but it has a shorter span-to-depth ratio of a composite specimen. While deforming, the maximum shear stress, which can be generated by combination of the compression on the top of the specimen and the tensile on the bottom of it, occurs at the mid-plane of the specimen. As a result, cracks are normally initiated and propagated by interlaminar shear failure.

Consequently, the objective of this work is preliminarily to investigate the effects of fiber surface-treatment and sizing

on the dynamic mechanical properties of unidirectional and 2-directional (woven fabric type) carbon fiber/nylon 6 composites using DMA. Also, the ILSS values measured for 2-directional carbon/nylon 6 composites sized with different thermosets and thermoplastics are compared.

2. Experimental

2.1. Materials

PAN-based carbon fibers and fabrics were used for studying surface-treatment and sizing effects, respectively. Continuous carbon fibers (IM7), supplied from Hercules, U.S.A., are of 6000 filaments and each filament has an average fiber diameter of 5 μm. Carbon fabrics with 8 harness satin texture, supplied from Tae Kwang Industries. Co., Korea, are of 3000 filaments and each filament has an average fiber diameter of 6.8 μm. The IM7 carbon fibers used in the present study were proprietarily surface-treated by the manufacturer but detail information on it has not been released. Only information we have is that the fibers were prepared with different surface-treatment (ST) levels like 0%, 20%, 100%, and 400% [13]. Here, 100% means typical ST level for commercial IM7 fiber production. Therefore, 0% means 'untreated', 20% 'one-fifth level' of commercial ST, and 400% 'four-fold level' of commercial ST. The IM7 fibers were used as received without further surface-treatment and sizing. 'As-received' carbon fabrics were commercially surface-treated but unsized. Pellet-type nylon 6 (Grade MC100L), supplied from Kanebo Gohsen, Ltd, Japan, was used as matrix resin. All fibers and nylon 6 pellets used in this work were dried at about 100°C before use. The information on the sizing materials used for carbon fabrics in the present work is given in Figure 1 and Table 1, respectively. A sizing concentration of 1 wt% solution of each polymer was applied on the commercially surface-treated carbon fabrics by a dip-coating manner and then dried, as indicated in Table 1, prior to composite fabrication.

2.2. Composite Preparations

Nylon 6 films were made with the pellets in between two smooth steel plates using a hot-press. The films were interleaved between the unidirectionally aligned carbon fiber layers in a steel mold. Unidirectional (UD) IM7 carbon fiber/nylon 6 composites were fabricated by a compression molding method using a hot-press. The molding condition was 230°C for 2 min with a pressure of 900 psi. The average thickness of UD carbon/nylon 6 composites obtained is 0.11

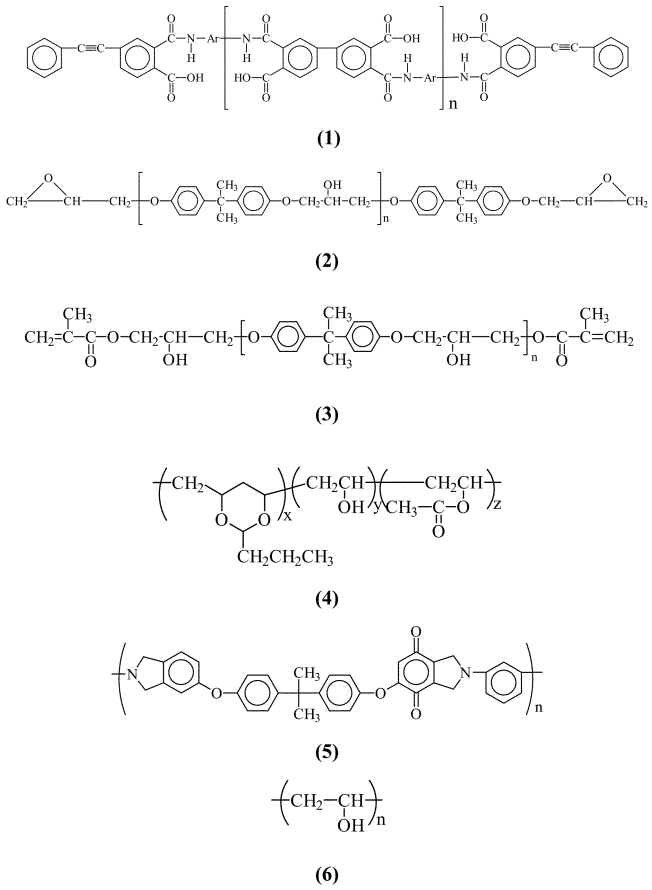

Fig. 1. Chemical structures of six sizing materials used for carbon fibers and fabrics in this work. (1) Phenylethynyl-terminated poly(amic acid), (2) Epoxy resin (Curing agent; Diethylenetriamine), (3) Vinyl ester resin (Catalyst: Methyl ethyl ketone peroxide, Accelerator: Cobalt naphthenate), (4) Poly(vinyl butyral-*co*-vinyl alcohol-*co*-vinyl acetate), (5) Polyetherimide, and (6) Poly(vinyl alcohol).

Table 1. Summarized information on the sizing materials used in this study

Sizing Material	Abbreviation	Trade Name	Supplier	Solvent	Dry Temp. (°C) After Sizing
Epoxy (DGEBA)	Epoxy	D.E.R. 383J-A90	Pacific Epoxy Co.	Methanol	70
Vinyl Ester	VE	SR-825L	Sewon Chemical Co.	Dimethylformamide	150
Poly(amic acid)	PETI-5	LaRC PETI-5	NASA, USA	*N*-methyl-2-pyrrolidinone	150
Poly(vinyl alcohol)	PVA	N/A	Aldrich	Water	90
Poly(vinyl butyral)*	PVB	N/A	Aldrich	Ethanol	80
Polyetherimide	PEI	Ultem 1000	GE Plastics	Dimethylformamide	150

*Poly(vinyl butyral-*co*-vinyl alcohol-*co*-vinyl acetate. N/A: Not available.

mm. The fiber contents are controlled to be 38% by weight. Two-directional (2D) carbon fabric/nylon 6 composites were also fabricated by film stacking and then compression molding methods using a hot-press. The same molding condition was used. The dimensions of 2D carbon/nylon 6 composites obtained were 22.0 mm × 10.0 mm × 2.18 mm and the fiber contents are controlled to be 39% by weight.

2.3. Analysis

Dynamic mechanical properties of each composite specimen were investigated using a dynamic mechanical analyzer (DMA 983, TA Instrument). A single cantilever bending mode was utilized with a sinusoidal frequency of 1 Hz and an oscillation amplitude of 0.20 mm. Each measurement was conducted from ambient temperature to 230ºC with a heating rate of 2ºC/min purging a N_2 gas of 50 cc/min. Short-beam shear tests for 2D carbon/nylon 6 composites were performed according to ASTM-2344 using a universal testing machine (Instron 4467). A crosshead speed of 1.3 mm/min was used. The span-to-depth ratio was 4:1.

3. Results and Discussion

3.1. Fiber Surface-Treatment Effect

Figure 2 shows the variation of the storage modulus (E') as a function of temperature measured for various strip-type UD carbon/nylon 6 composite specimens with different ST levels. The nylon 6 specimen without reinforcing fibers exhibits the lowest log E' value over the whole temperature range. The higher log E' value of the composite specimens is due to carbon fiber reinforcement effect. The storage modulus of 0% ST composite is the greatest, reflecting that the untreated one has the greater dynamic mechanical property than the surface-treated ones. This is probably that the fiber surface with crystalline structure may be slightly damaged by surface-treatment process. The storage modulus of 100% ST carbon/nylon 6 composite is slightly greater than that of 20% ST counterpart. This may be ascribed to an increase of the interfacial adhesion between the fibers and the matrix resin, resulting from an increase of oxygen-containing chemical groups on the fiber surface by the treatment, even though the surface may be somewhat damaged by the ST. The composite specimen with 400% ST carbon fibers shows the lowest log E' value among the treated ones. This may be explained by that IM7 carbon fiber surfaces may be profoundly damaged by excessive ST and, in addition, a large number of oxygen-containing groups generated by the ST process may more or less reduce the stiffness of the composite although the functional groups on the surface may also somewhat contribute to enhancing the interfacial bonding between the fibers and the matrix in the composite.

In Figure 3, the tan δ peaks in the range of 60ºC~80ºC of each curve indicate the glass transition temperature (T_g) of

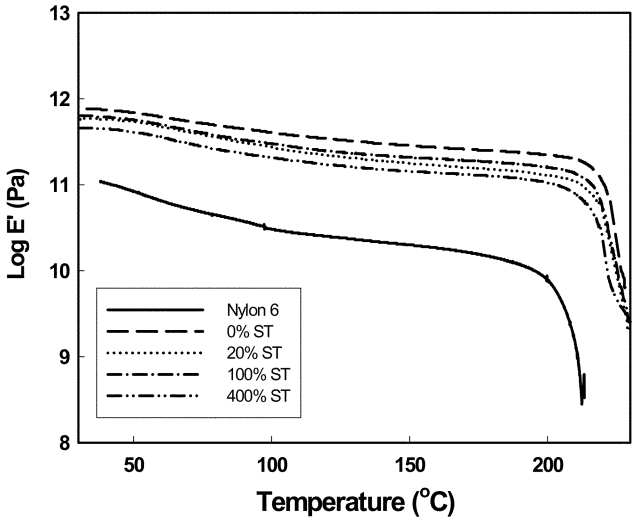

Fig. 2. Variations of the storage modulus as a function of temperature for nylon 6 and unidirectional carbon fiber/nylon 6 composites with various surface-treatment levels.

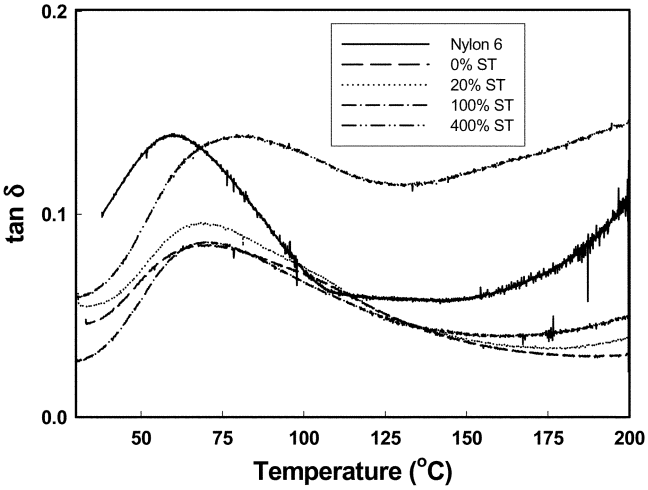

Fig. 3. Variations of the tan δ as a function of temperature for nylon 6 and unidirectional carbon fiber/nylon 6 composites with various surface-treatment levels.

UD carbon/nylon 6 composite. It is observed that the T_g of nylon 6 is about 60ºC. The T_g of the composites is greater than that of nylon 6 because the presence of reinforcing fibers surrounded by the matrix significantly restricts the molecular mobility of the resin. The tan δ result may indirectly imply that the interfacial adhesion increases with increasing the ST level. The T_g values determined from the tan δ peak temperature are increased from 0% ST (69ºC) to 400% ST (79ºC) through 20% ST (70ºC) and 100% ST (73ºC). This result agrees with earlier reports that the T_g increases with increasing the fiber-matrix interfacial adhesion in a composite and the interfacial adhesion is enhanced with surface-treatment effectiveness on carbon fiber [9, 13]. Oxygen-containing

Table 2. A summary of the glass transition temperatures and the storage moduli obtained from the DMA result for 2D carbon/nylon 6 composites sized with different thermosetting and thermoplastic materials

Characteristics	Thermosetting			Thermoplastic		
	Epoxy	VE	PETI-5	PVA	PVB	PEI
T_g (°C)	78	87	66	78	71	77
E (GPa) at T_g	21.4	22.5	21.4	19.9	18.5	20.4
E(GPa) at 180°C	12.9	12.9	15.8	12.6	12.8	14.1

functional groups on the carbon fiber surface increase with ST level by liquid-phase oxidation, contributing to an increased interaction at the interfaces between the fibers and the matrix resin [4].

3.2. Fiber Sizing Effect

Table 2 summarizes the T_g and the E values at T_g and 180°C from the plots of storage modulus and tan δ as a function of temperature measured for 2D carbon fabric/nylon 6 composites sized with various polymer solutions at a fixed concentration of 1 wt%, respectively. The nylon 6 used here has a T_g of about 60°C. In this work, the T_g of 2D carbon/nylon 6 composite made with the desized fabrics was not measured because desizing process may influence the surface characteristics of commercially surface-treated fabrics. However, it is noted from the result in Figure 3 that a carbon/nylon 6 composite fabricated with surface-treated but unsized IM7 carbon fibers has a T_g of about 72°C.

As can be seen, the composite specimen fabricated using carbon fabrics sized with vinyl ester (VE) resin has the greatest T_g. One possible reason for the increased T_g in the composites sized with VE is that there may be a strong amino-vinyl reaction between the amino groups in nylon 6 and the unsaturated double bonds in VE, considering nucleophilicity and the unshared electron pair in the amino group [12]. In addition, it is expected that VE can be fully cured at the temperature for processing a carbon/nylon 6 composite accompanying some possible interdiffusion between the matrix resin and the sizing interphase before complete cure. Such the behavior may contribute to enhancing the interfacial bonding between the fibers and the matrix in the composite. As a result, the E' value at T_g in the VE case is greater than in other cases. Epoxy and PVA are frequently used as sizing material [14]. Also, it is generally known that they play an effective role in binding between two intimate materials including the fibers and the matrix of a composite. The composites sized with epoxy and PVA show similar T_g and E' values but the lower values than the VE case.

The low T_g of the composite sized with PETI-5 is because PETI-5 was only partially cured at the dry condition of 150°C and the composite processing temperature of 230°C [15]. For compete cure, PETI-5 needs 350°C or higher [16,17]. In fact, cured PETI-5 is strong, tough, and high-temperature resistant polymer with a T_g of about 280°C or higher. It has been reported that PETI-5 may be used as a high-temperature sizing material for a carbon fiber-reinforced thermosetting matrix composite system as this material forms an interphase interdiffused with the matrix resin and then has a fully cured structure [6]. However, it is not appropriate to be utilized as a sizing material in the present thermoplastic composite system, which has a composite processing temperature lower than the cure temperature of PETI-5. It is known that PEI, which is an amorphous engineering thermoplastic and maintains properties at elevated temperature, has a T_g of about 216°C [18]. The processing temperature is about 350°C, which is much higher than that for making a carbon/nylon 6 composite. The T_g value of the composite is lower than expected, as described in the case of PETI-5. However, the storage moduli of the composites sized with PETI-5 and PEI are relatively higher than others, especially at 180°C.

The composite sized with PVB exhibits the lowest T_g. PVB is a random copolymer containing vinyl alcohol and vinyl acetate moieties with a T_g of about 72°C~78°C depending on the copolymer composition. This T_g is the lowest among the sizing materials used here. This is mainly responsible for the low T_g value of the composite sized with PVB. The composite also shows the lowest E value at T_g. It is noted that PVB is commonly utilized as the adhesive layer of laminated safety glass due to excellent adhesion to glass [19]. Therefore, it may be expected that PVB probably contribute to some extent to increasing the interfacial adhesion in the present composite system. At 180°C, the E' values are observed to be comparable, with the exceptions of PETI-5 and PEI, which are thermally stable at elevated temperature.

Figure 4 compares the interlaminar shear strengths (ILSS) for 2D carbon fabric/nylon 6 composites sized with various materials, as mentioned in Table 2. The short-beam shear testing was done with removing the applied load as soon as the initial delamination between the fiber and the matrix takes place through the thickness in a composite right after the yield point in the stress-strain behavior. The averaged ILSS values were obtained from the maximum load of the load-displacement curve for each specimen using the following equation.

$$\tau_{max} = 3P_{max}/4b \cdot t$$

where τ_{max} is the ILSS, P_{max} is the maximum load, b is the width of the specimen, and t is the thickness of the specimen.

As can be seen, the ILSS value of the composite sized with VE is the highest among the tested specimens. It is even higher than the composite fabricated with commercially sized fabrics although its sizing information has not been known at all, unfortunately. The commercial one shows a higher ILSS than other materials beside VE. It may be speculated that the commercial carbon fabrics used here probably contain a

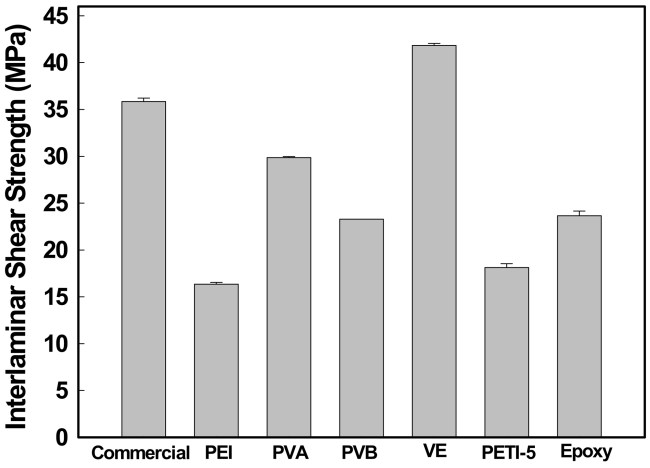

Fig. 4. A comparison of the interlaminar shear strengths for 2-directional carbon fabric/nylon 6 composites treated with various sizing materials.

sizing concentration higher than 1 wt% and also other chemical components for making weaving process easy. The 2D carbon/nylon 6 composites sized with PVA, epoxy and PVB have a relatively higher ILSS value than the counterpart with PETI-5 and PEI. This ILSS result more or less has a comparable tendency with that found in the dynamic mechanical result.

The dynamic mechanical and the short-beam shear test results indicate that appropriate use of a sizing material upon carbon fiber composite processing may contribute to enhancing the interfacial and/or interlaminar properties of carbon/nylon 6 composites resulting in an increase of T_g and storage modulus, relying on the resin characteristics and the processing temperature. It is also suggested that as one has detail information on sizing processing including concentration and composition, the interfacial properties of a carbon fiber composite system may be further improved.

4. Conclusion

The carbon fiber surfaces used in the present study may be significantly damaged by excessive surface-treatment and a large number of oxygen-containing groups generated by the treatment may more or less reduce the stiffness of carbon/nylon 6 composite although the functional groups on the surface may also somewhat contribute to enhancing the interfacial bonding between the fibers and the matrix in the composite. The T_g of the composite increases with increasing the fiber-matrix interfacial adhesion and the interfacial adhesion is enhanced with surface-treatment effectiveness on carbon fiber. The dynamic mechanical and the short-beam shear test results indicate that appropriate use of a sizing material upon carbon fiber composite processing may contribute to enhancing the interfacial and/or interlaminar properties of carbon/nylon 6 composites, depending on their resin characteristics and processing temperature.

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