論文

Enhanced Interfacial Adhesion of Carbon Fibers by Poly (arylene ether phosphine oxide) Coatings

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Poly(arylene ether phosphine oxide) 코팅에 의한 탄소섬유의 계면 접착성 향상 연구

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초 록

Poly(arylene ether phosphine oxide)(PEPO)로 코팅된 탄소섬유의 계면접착력을 microdroplet 시험으로 측정하였으며, 이결과를 poly(arylene ether sulfone) (PES), Udel® P-1700 and Ultem® 1000으로 코팅된 탄소섬유의 결과와 비교하였다. 또한 코팅에 사용된 고분자와 탄소섬유와의 계면접착력을 탄소섬유와 고분자의 접착 메카니즘을 규명하기 위하여 측정하였다. PEPO로 코팅된 탄소섬유가 가장 높은 계면접착력을 보였으며, Udel, PES 그리고 Ultem 고분자 코팅 순으로 감소하였다. 고분자와 탄소섬유의 계면접착력 또한 비슷한 경향을 보였다. SEM 분석결과 PEPO로 코팅된 탄소섬유에서는 비닐에스터 수지 내에서 파괴가 일어난 것으로 보여지나, 다른 고분자로 코팅된 탄소섬유에서는 계면 또는 계면에서 가까운 곳에서 파괴가 일어난 것으로 판단된다. PEPO 코팅에 의한 계면접착력 향상은 PEPO내에 존재하는 P = O 때문으로 사료된다.

ABSTRACT

Interfacial shear strength (IFSS) of poly(arylene ether phosphine oxide) (PEPO) coated carbon fibers was evaluated via microdroplet tests and compared with results obtained from carbon fibers coated with poly(arylene ether sulfone) (PES), Udel® P-1700 and Ultem® 1000. Interfacial adhesion between thermoplastics and uncoated carbon fibers was also measured in order to understand the adhesion mechanism. PEPO coated carbon fibers showed the highest IFSS, followed by PES, Udel and Ultem coated fibers. A similar trend was observed for thermoplastic/uncoated fibers. SEM analysis indicated that only PEPO coated fiber exhibited cohesive failure in the vinylester resin, while others showed failure at or near the interface of polymer coating and vinylester resin. The enhanced interfacial adhesion by PEPO coating could be attributed to the strong interaction of P = O moiety to the fiber as well as to the vinylester resin.

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1. Introduction

Vinylester resins are one of the well known thermoset resins in composite applications due to their low cost, low viscosity and excellent corrosion resistance, promoting their use in glass fiber reinforced composites for automotive applications [1]. Recently, there has been an increasing demand for vinylester resin composites for infrastructures such as bridges [2]. However, poor interfacial adhesion of vinylester resins to reinforcing fibers such as glass, carbon and organic fibers has been a major obstacle to the wider application of vinylester resins.

A number of researchers have investigated the governing factors of interfacial adhesion between fiber and matrix [3-5], and suggested fiber surface modification by corona discharge and plasma treatment, surface oxidation or polymer coatings [6-8] to improve interfacial adhesion. There has also been a number of studies on enhancing the interfacial adhesion of vinylester/glass fibers [9, 10] and vinylester/Spectra fibers [11], but only few on vinylester/carbon fibers [12].

Recently, fiber surface modification by polymer coatings has received much attention since it can improve not only interfacial adhesion but also toughness at the interface. In this study, it was attempted to improve the interfacial adhesion of carbon fibers by coating their surface with high performance thermoplastics such as poly(arylene ether phosphine oxide) (PEPO) which is known to have excellent adhesive properties as well as mechanical and thermal properties (13-14). Poly(arylene ether sulfone) (PES), Udel® P-1700 and Ultem® 1000 were also utilized for comparison purposes.

The interfacial shear strength (IFSS) between vinylester and thermoplastic coated carbon fibers was evaluated by microdroplet tests. Interfacial adhesion between carbon fibers and thermoplastics was also measured in order to elucidate the adhesion mechanism between thermoplastics/carbon fibers and carbon fibers/vinylester resins. The surfaces of thermoplastic coated carbon fibers were analyzed by SEM and correlated to the pull-out curves in order to understand the locus of failure and thus the adhesion mechanism.

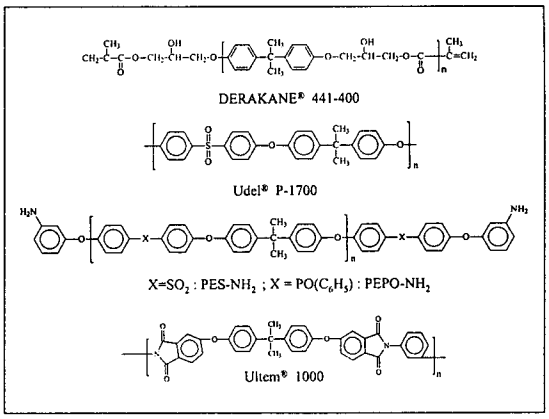

Fig. 1. Chemical structure of polymers for fiber

2. Experimental

2.1 Materials

DERAKANE 441-400 vinylester resin (Dow Chemical Co.) was used as received and benzoyl peroxide (Aldrich Chemicals) was used as an initiator. Poly(arylene ether phosphine oxide) (PEPO) and poly(arylene ether sulfone) (PES) were synthesized in our laboratory, and their molecular weights were controlled to 20,000 g/mole. Commercial polymers such as Udel® P-1700 and Ultem® 1000 were provided by Amoco and GE, respectively.

The chemical structure of the polymers are shown in Fig. 1 and their detailed synthesis is found elsewhere [15]. Unsized AS-4 carbon (Hercules Inc.) fibers with an average diameter of 8㎛ were used as received or after thermoplastic coating, which was performed by dipping a single carbon fiber into a 1wt.% solution in chloroform for 1 minute, followed by drying at 100℃ for 12 hours. The concentration (1, 2, 3 wt.%) of solu-

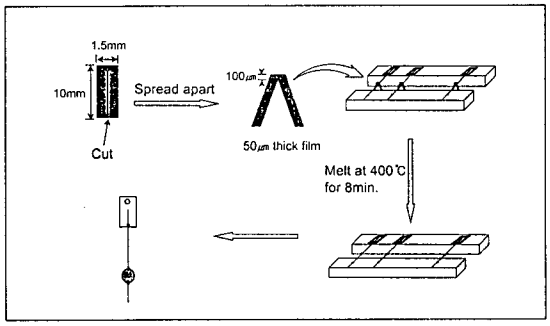

Fig. 2. Preparation of microdroplet specimen with thermoplastic polymer

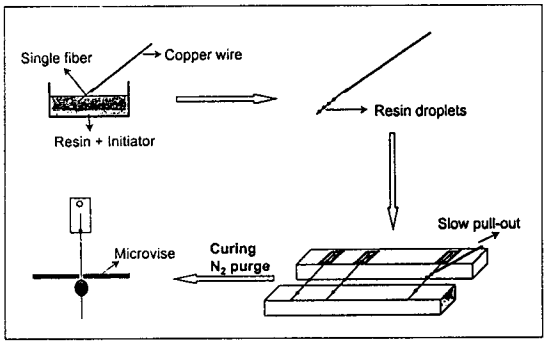

Fig. 3. Preparation of microdroplet specimen with vinylester resin

tion and dipping time (1, 2, 3 min) were also optimized.

2.2 Cure Study

Cure conditions for vinylester resins were optimized by differential scanning calorimeter (DSC 2010, TA Instrument). Since the oxygen in the resin is known to be a radical scavenger, it was removed by the freeze/thaw technique to afford complete cure. 1.1 wt.% of benzoyl peroxide was added into vinylester resin and stirred at room temperature until a clear mixture was obtained. The mixed resin was poured into a silicone rubber mold which was preheated to 90, 120, 130 or 140 ℃, and cured at that temperature for 10, 20, 30 or 60 minutes. The cured samples were characterized by DSC at a heating rate of 10℃/minute under nitrogen purge and their Tg and degree of cure were measured.

2.3 Preparation of Microdroplet Samples

The microdroplet specimens of thermoplastic/carbon fiber were prepared by the procedure described by Commercon (16). A single carbon fiber was placed on the aluminum fixture, and a piece of polymer film with the thickness of approximately 50㎛ and the size of 10mm × 1.5mm was hung on the single carbon fiber (Fig. 2). The microdroplet was formed by heating in an oven at 400℃ for 5-8 minutes. The size of the microdroplet was measured by SEM and used to calculate the interfacial shear strength.

Unlike thermoplastics, vinylester resins are liquid at room temperature, and thus microdroplets were prepared by the solution method (16). A series of droplets were formed by dipping a short single fiber into the resin then pulling. One of the resin droplet was transferred to the single carbon fiber on the aluminum fixture by contact (Fig. 3). The samples were cured under N_2 atmosphere by the optimized cure cycle.

2.4 Measurement of Interfacial Adhesion

Interfacial shear strength was measured with Instron 5567 at a speed of 0.3mm/minute. Since the debonding load was too low to be measured by Instron 5567, a balance (BB 2400, Mettler) connected to a personal computer was utilized as published (16). The interfacial shear strength was calculated from the following equation :

$$\tau = \frac{F_d}{\pi d_f L}$$

where F_d is the maximum debonding load, d_f is the fiber diameter and L is the embedded fiber length in a droplet. At least 50 specimens were tested and the results were averaged.

3. Results and Discussion

3.1 Optimum Cure Condition

From the DSC analysis, it could be seen that the cure reaction was not complete even after 60 minutes at 90℃ (Table 1). However, complete cure was achieved by 30 minute cure at 120℃, and by 10 minute cure at 130℃ as well as at 140℃, exhibiting a Tg of 140℃. The cure reaction at or above 140℃ was not desirable due to the large loss of styrene monomers during the curing process. As a result, curing at 130℃ for 20 minutes was selected as the optimum condition to ensure complete cure and to minimize the loss of styrene monomers.

3.2 Interfacial Adhesion with Polymer Coated Carbon Fibers

The microdroplets, prepared with vinylester resin on polymer coated carbon fibers, were ellipsoidal with length ranging from 80 to 120 ㎛. The angle between the fiber and the edge of microdroplet seemed to decrease as the coated polymer changed from Ultem, PES or Udel to PEPO. This may be related to the wetting behavior of vinylester on the polymer coated fibers.

The optimum concentration and dipping time for PEPO and Udel polymer were 1 wt.% and 1 minute, respectively. As they increased, the interfacial shear strength slightly decreased possibly due to the increased coating thickness. As expected, the samples from PEPO coated carbon fibers showed the highest interfacial shear strength of 56 MPa, followed by PES (46 MPa), Udel P-1700

Table 1. Optimized cure condition for vinylester resin

Time / Temp.	Degree of cure			
	10min.	20min.	30min.	60min.
90℃	79%	87%	93%	96%
120℃	98%	99%	(140℃)	(140℃)
130℃	(136℃)	(140℃)	(139℃)	–
140℃	(140℃)	–	–	–

( ) : Tg measured by DSC (TA 2050) at 10℃/min

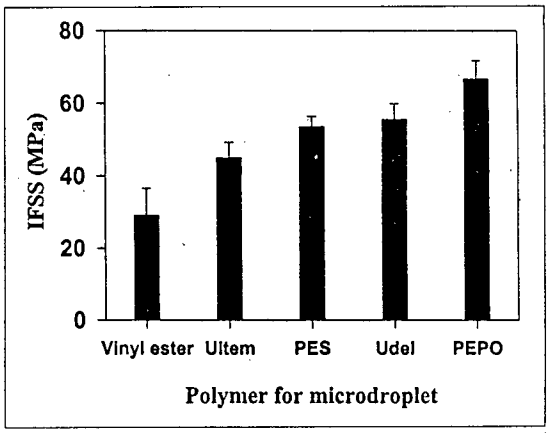

Fig. 4. Interfacial shear strength of polymer coated fibers/ vinylester resin

(44 MPa) and Ultem 1000 (29 MPa) coated fibers as shown in Fig. 4. Compared to these values, the control sample from vinylester/unsized carbon fiber provided interfacial shear strength (IFSS) of 30 MPa, indicating poor interfacial adhesion.

The interfacial shear strength of carbon fibers was enhanced by PEPO, Udel P-1700 and PES coating, but not by Utem 1000. As reported (14), this could be explained by the functional groups such as phosphine oxide moiety in PEPO and sulfone groups in Udel P-1700 and PES, which can increase interfacial adhesion. Unfortunately, Ultem 1000 lacks such a group in its chemical structure.

The failure surface of PEPO coated carbon fibers was almost fully covered by polymer which might be vinylester resin (Fig. 5), indicating strong adhesion not only between PEPO coating and carbon fibers, but also between PEPO coating and vinylester resin. However, the failure surface of carbon fibers coated with Udel, PES and Ultem was smooth but was somewhat different from the surface of as-received fibers (Fig. 5). Furthermore, it was not possible to determine the location of the microdroplets. Therefore, it was assumed that the interfacial failure had occurred at the interface of polymer coating and vinylester resin.

The samples prepared from Udel, PES and Ultem coated fibers showed approximately

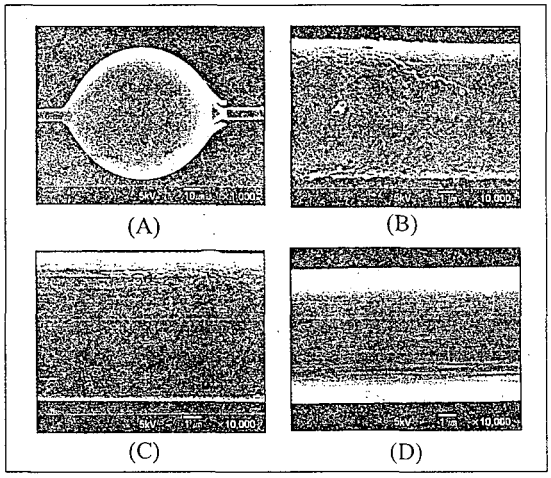

Fig. 5. SEM micrographs of microdroplet and polymer coated carbon fiber after testing. (A) microdroplet of vinylester (B) PEPO coated carbon fiber, (C) Udel coated carbon fiber, and (D) Ultem coated carbon fiber

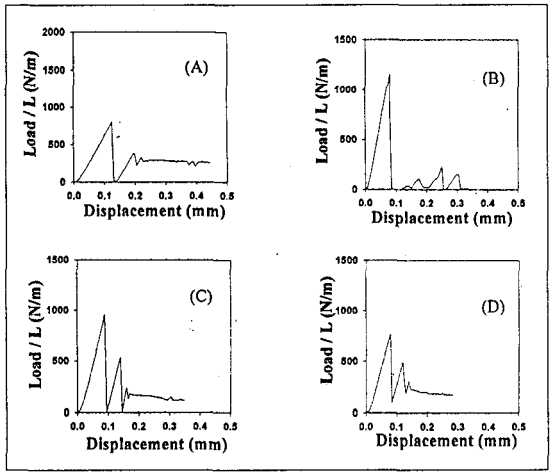

Fig. 6. Typical load versus displacement curves from the samples with polymer coated fibers and vinylester resin; (A) uncoated carbon fiber, (B) PEPO coated carbon fiber, (C) Udel coated carbon fiber, (D)Ultem coated carbon fiber

20g/mm of load in the stick-slip region, compared with 30g/mm in the control sample, indicating relatively high friction force (Fig. 6).

However, PEPO coated fiber samples which had polymer layer on the surface exhibited less than 10g/mm of load in the stick-slip region. The friction force in the stick-slip region could be related to the hole diameter in the droplet.

If debonding had occurred at the fiber/polymer coating interface, the hole diameter in the microdroplet would be almost the same size as the fiber diameter, resulting in a high load in the stick-slip region (PES, Udel and Ultem coated fibers). On the other hand, if debonding had occurred in the vinylester resin, leaving vinylester layer on the fiber surface, a low stick-slip load would be generated, due to the larger hole diameter in the microdroplet compared to the fiber diameter (PEPO coated fibers).

3.3 Interfacial Adhesion with Polymer and Carbon Fibers

The interfacial adhesion between thermoplastic polymers and carbon fibers was evaluated in order to elucidate the adhesion mechanism. The shape of the microdroplet was ellipsoidal, 70-90㎛ in length, and was smaller than the ones formed with vinylester resin on thermoplastic coated fibers.

The interfacial shear strength (IFSS) of PEPO/carbon fiber was 67 MPa, which was higher than that of PEPO coated carbon fiber with vinylester resin.

Udel® P-1700/carbon fiber, PES/carbon fiber and Ultem® 1000/carbon fiber provided IFSS of 56, 50 and 45 MPa, respectively (Fig. 7). This again could be attributed to the phosphine oxide group in PEPO, as discussed previously. It can

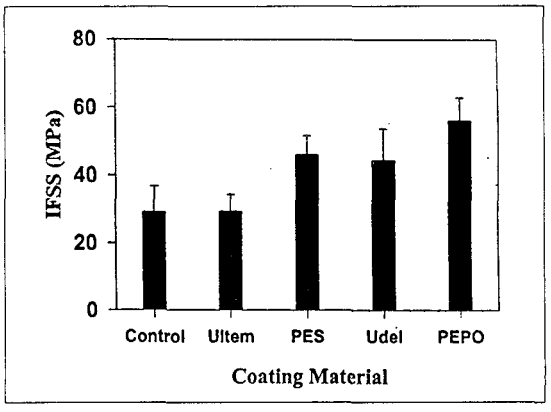

Fig. 7. Interfacial shear strength from carbon fibers and polymers

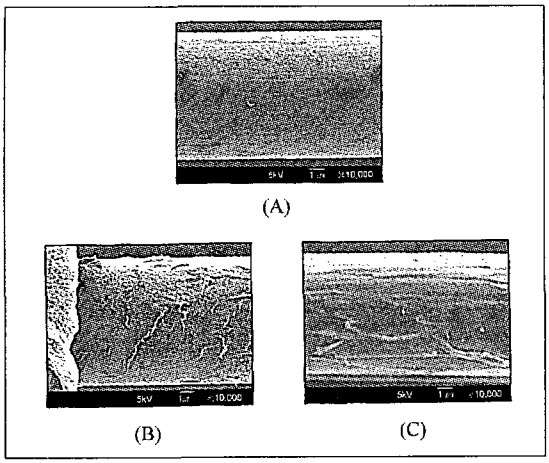

Fig. 8. SEM micrographs of carbon fiber surface after testing; (A) vinyl ester/uncoated carbon fiber, (B) PEPO/uncoated carbon fiber, (C) Udel/uncoated carbon fiber

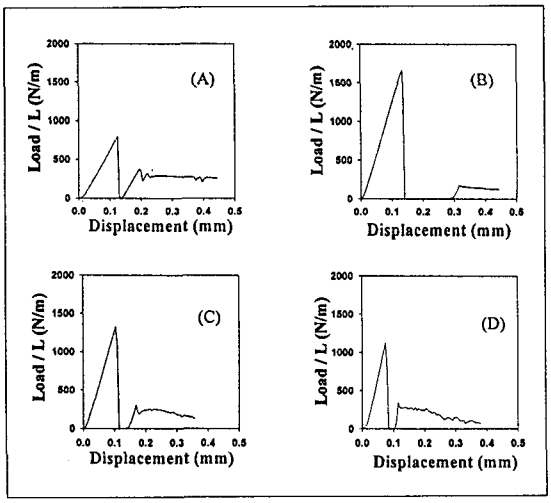

Fig. 9. Typical load versus displacement curves from polymer/unsized carbon fiber, (A) vinylester, (B) PEPO, (C) Udel, (D) Ultem

also be noted that the polymer droplet samples exhibited higher IFSS than polymer coated fiber samples, indicating better adhesion between carbon fibers and polymer than between polymer and vinylester resin or between carbon fibers and vinylester resin.

The carbon fibers from PEPO droplet samples showed fully covered polymer layer on the fiber surface (Fig. 8). This result indicated that the failure had occurred in the PEPO layer and thus good adhesion between fiber and PEPO. The low fraction force in the stick-slip region also support good adhesion, as explained in the previous section (Fig. 9). However, the fibers from PES, Udel and Ultem droplet samples did not show polymer layers on their surface, which was much rougher than the as-received fibers. Therefore, it is believed that the failure had occurred near the fiber/polymer interface.

4. Conclusions

The interfacial shear strength of carbon fiber/vinylester was investigated as a function of the structure of coated polymer on carbon fibers via microdroplet tests. Major findings are summarized below:

1. The interfacial shear strength (IFSS) of vinylester/carbon fiber was greatly increased by PEPO coating, followed by Udel, PES and Ultem coatings.

2. SEM analysis revealed that only PEPO coated fiber samples exhibited cohesive failure in the vinylester layer which was further supported by the low friction force in the stick-slip region

3. Increased IFSS with PEPO coating can be attributed to the phosphine oxide group which provided strong adhesion not only to carbon fiber, but also to vinylester resin.

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