

계면 확산에 의한 고분자 코팅된 탄소섬유의 계면접착력 변화 연구

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Effect of Diffusion on the Adhesion Behavior of Polymer Coated Carbon Fibers with Vinyl Ester Resins

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Key Words : interfacial adhesion, vinyl ester resin, carbon fiber, polymer coating, micro-droplet test, solubility, miscibility

ABSTRACT

Poly(arylene ether phosphine oxide) (PEPO), Udel[®] P-1700, Ultem[®] 1000, poly(hydroxy ether) (PHE), carboxy modified poly(hydroxy ether)(C-PHE) and poly(hydroxy ether ethanol amine) (PHEA) were utilized for a coating of carbon fibers. Interfacial shear strength(IFSS) of polymers to carbon fibers was also evaluated in order to understand the adhesion mechanism. IFSS was measured via micro-droplet tests, and failure surfaces were analyzed by SEM. Diffusion between polymer and vinyl ester resin was investigated as a function of styrene content; 33, 40 or 50wt.% and the solubility parameters of polymers were calculated. The results were correlated to the interfacial shear strength. The highly enhanced interfacial shear strength (IFSS) was obtained with PEPO coating, and marginally improved IFSS with PHE, Udel[®] and C-PHE coatings, but no improvement with PHEA and Ultem[®] coatings.

1. INTRODUCTION

Vinyl ester resin is one of the widely utilized thermoset resins for composites and coatings applications due to their good electrical and mechanical properties, and excellent corrosion resistance (1-2). Recently, there has been an great interest in vinyl ester resins for infra-structural composites applications such as bridges due to their good processability and mechanical properties. Since performance of composites materials are strongly dependent on the interfacial adhesion between fibers and matrix resin (3-4), surface of reinforcing fibers has to be properly tailored to achieve maximum adhesion.

Polymer coatings for carbon fiber surface modification have received a great attention due to their advantages such as enhanced interfacial adhesion as well as improved toughness at the interface. Recently, poly(vinylpyrrolidone) (5), poly(arylene ether phosphine oxide) (6), polyurethane(7) were successfully utilized to enhance the interfacial adhesion of carbon fiber to vinyl ester resin.

In this study, carbon fibers were coated with thermoplastic polymers in order to enhance the interfacial adhesion to vinyl ester resin. Diffusion behavior between polymers coating and vinyl ester resin was investigated via SEM analysis and correlated to the interfacial adhesion and the structure of polymers.

2. EXPERIMENTAL

Materials

The vinyl ester resin with 33 wt. % styrene (DERAKANE 441-400) was friendly donated by Dow Chemical, and styrene monomer (Junsei) and benzoyl peroxide (Aldrich) were purchased. Poly(arylene ether phosphine oxide) (PEPO) with molecular weight of 20,000 g/mole was synthesized in our laboratory as reported elsewhere (11-12) and commercial polymers such as Udel® P-1700 and Ultem® 1000 were provided by Amoco and GE, respectively (Figure 1). A water soluble carboxy modified poly(hydroxy ether) (C-PHE) from Phenoxy Assoc. (Rock Hill, SC, U.S.A) and water insoluble poly(hydroxy ether ethanolamine) (PHEA) from Dow) and poly(hydroxy ether) (PHE) from Phenoxy Assoc., were also utilized. Unsized AS-4 carbon fibers from Hercules with an average diameter of 8 μ m were used for polymer coating.

Interfacial adhesion study

Coating of carbon fibers with PEPO, Ultem® or Udel® was carried out by dipping a single carbon fiber into a 1wt. % solution in chloroform for 1 minute, followed by drying at 100°C for 12 hours. Since C-PHE was water-soluble, 2wt. % aqueous solution was utilized to coat carbon fiber by dipping. However, PHE and PHEA were water-insoluble. 2wt. % solution in THF or aqueous acetic acid, respectively, was used for dip-coating of fibers, followed by drying at 100°C for 12 hours.

Micro-droplet specimens were prepared by the liquid method for vinyl ester droplet or film method for polymer droplets as described previously (6, 9). Micro-droplets of polymers, however, were prepared by melting a piece of polymer film hanged on a carbon fiber as reported (6). The size of the micro-droplets was measured by SEM and used for the calculation of interfacial shear strength.

Interfacial shear strengths of micro-droplets were measured with Instron 5567 at a speed of 0.3mm/minute. Since the loads from the test was so small, a micro-balance (BB 2400, Mettler) connected to a personal computer was utilized to measure debonding load. The interfacial shear

strength was calculated with the following equation:

$$IFSS = F_d / d_f L$$

where F_d is a maximum debonding load, d_f is a fiber diameter and L is the embedded fiber length in a droplet. At least 30 specimens were tested and the results were averaged.

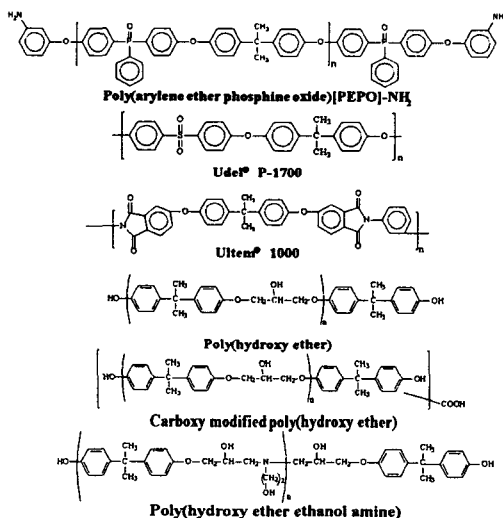


Figure 1. Chemical structure of polymers - PEPO, Udel, Ultem and Poly(hydroxy ether)s

Diffusion Study

The samples for diffusion study were prepared from a piece of film and vinyl ester resin. An extra styrene monomer was added to DERAKANE 441-400 which already contained 33wt % of styrene monomer to afford 40 and 50 wt % styrene in order to understand the role of styrene in diffusion. The specimens (3x6x15mm) for diffusion study were prepared by inserting polymer films into vinyl ester resin in silicon rubber mold, followed by curing at 130°C for 20min.

3. RESULTS AND DISCUSSIONS

Interfacial Adhesion of Polymer to Carbon Fibers

The interfacial adhesion of polymers to carbon fibers was evaluated in order to understand the adhesion mechanism between polymer coating and fiber. The prepared micro-droplet size was 40-80 μ m. The interfacial shear strength with C-PHE could not be measured since it did not melt even

at 400°C but degraded. The interfacial shear strength with PEPO was 66.7 ± 4.8 MPa, which was followed by Udel® (55.6 ± 4.3 MPa), PHE (55.2 ± 6.7 MPa), PHEA (53.2 ± 7.4 MPa) and Ultem® (45.0 ± 4.3 MPa).

Interfacial Adhesion with Polymer Coated Carbon Fibers

The micro-droplets prepared from vinyl ester resin and polymer coated carbon fibers were ranged from 40 to 80 μm in length. As expected from polymer droplet studies, PEPO coating exhibited higher interfacial shear strength of 52.5 ± 7.2 MPa than PHE (45.3 ± 8.3 MPa), Udel® (42.9 ± 5.7 MPa), and C-PHE (41.3 ± 6.4 MPa) coating. However, PHEA (30.5 ± 9.4 MPa) and Ultem® (29.7 ± 10.2 MPa) coated carbon fibers exhibited as low IFSS as those with as-received carbon fibers (29.1 ± 7.5 MPa).

Diffusion Study

As shown in Figure 2, it was difficult to differentiate PEPO film from vinyl ester region, but only clue was surface roughness. However, the rough surface was not observed at 50wt % of styrene, suggesting that PEPO film completely dissolved in vinyl ester resin (before cure), and is completely miscible with vinyl ester resin (after cure), which could be due to strong interaction by phosphine moiety as reported (6). Therefore, highest IFSS with PEPO coating can be attributed to excellent solubility and miscibility of PEPO in vinyl ester resins.



Figure 2. SEM micrographs of diffusion layer of PEPO/vinyl ester resin. (A) 33wt.% styrene, (B) 40wt.% styrene

As shown in Figure 3, the samples with Udel® film, however, exhibited a distinct film region and somewhat clear interface between the film region and the vinyl ester region even at 50% styrene.

It is believed that Udel® film has limited solubility in liquid vinyl ester resin, if there is any, and reverse is true. However, vinyl ester

resins diffused into Udel® film (before cure), and formed spheres during the cure due to immiscibility with Udel®. High but inferior IFSS with Udel® coating to that with PEPO coating can be attributed to immiscibility of vinyl ester resin with Udel®, and limited solubility of Udel® in vinyl ester resin.



Figure 3. SEM micrographs of diffusion layer of Udel®/vinyl ester resin. (A) 33wt.% styrene ($\times 500$), (B) 33wt.% styrene ($\times 10,000$)

As shown in Figure 4, the Ultem® film region with sharp interface was observed. The diffused area of film region was very small (Figure 4-A), and even at 50% of styrene only half of film was diffused. At the high magnification, small spheres were observed as seen in the diffused part of Udel® samples (Figure 3-B). Thus Ultem® may not be soluble and miscible in vinyl ester resin. Therefore, very low IFSS with Ultem® coating can be explained by insolubility and immiscibility of Ultem® in vinyl ester resin, resulting in sharp interface and thus interfacial failure.

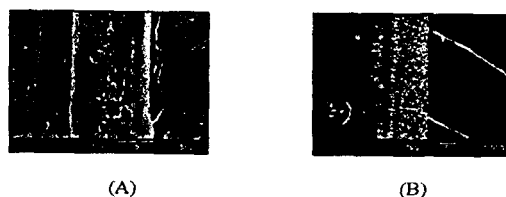


Figure 4. SEM micrographs of diffusion layer of Ultem®/vinyl ester resin (A) 33wt.% styrene ($\times 500$), (B) 33wt.% styrene ($\times 3,000$)

The samples with PHE showed clear film region, but inter-diffused interface (or interphase), indicating good mutual solubility in each other (Figure 5-A). Spheres were also seen in the edge of film region, exhibiting immiscibility of vinyl ester resin in the PHE region. At 40% of styrene, most of film was dissolved, and whole

film disappeared at 50% of styrene, suggesting good solubility of PHE in vinyl ester resin (Figure 5-B). Therefore, high but inferior IFSS with PHE coating to that with PEPO coating can be attributed to immiscibility.



Figure 5. SEM micrographs of diffusion layer of PHE/vinyl ester resin. (A) 33wt.% styrene ($\times 300$), (B) 50wt.% styrene ($\times 3,000$)

In C-PHE diffusion samples, inter-diffused interface (interphase), spheres in the film region, and film region was observed even at 50% styrene (Figure 6). However, major difference from other samples was mutual immiscibility between vinyl ester and C-PHE, showing spheres in inter-diffused region. Relatively high IFSS with C-PHE coating can be attributed to good inter-diffusion, but limited solubility and immiscibility of C-PHE in vinyl ester provided inferior IFSS to PEPO.



Figure 6. SEM micrographs of diffusion layer of C-PHE/vinyl ester resin. (A) 33wt.% styrene, (B) 50wt.% styrene



Figure 7. SEM micrographs of diffusion layer of PHEA/vinyl ester resin. (A) 33wt.% styrene, (B) 50wt.% styrene

The samples with PHEA showed very narrow

diffused region, but aggregate of spheres as observed from Udel[®] sample (Figure 7). As styrene content increased, inter-diffused layer slightly increased, but still very small. Therefore, it can be said that PHEA has very poor solubility and poor miscibility in vinyl ester resin, resulting in very low IFSS and smooth failure surface.

4. CONCLUSIONS

The interfacial shear strengths of carbon fiber/vinyl ester was evaluated via micro-droplet tests and adhesion mechanisms was investigated by diffusion study. The interfacial shear strength (IFSS) of PEPO with carbon fiber was highest, followed by Udel[®], PHE and CPHE, but no improvement was noticed with PHEA and Ultem[®]. PEPO film exhibited excellent solubility and complete miscibility with vinyl ester resin, showing high IFSS, while Udel[®], PHE and C-PHE showed low solubility but good miscibility, resulting in marginally improved IFSS. However, Ultem[®] and PHEA exhibited poor solubility in vinyl ester resin provided as same IFSS as control.

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