

Comparison of Electrodeposited Carbon Fibers Reinforced Epoxy Composites Using Monomeric and Polymeric Coupling Agents

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Abstract : By electrodeposition (ED) using a monomeric- and two polymeric coupling agents, the interfacial shear strength (IFSS) of carbon fiber/epoxy composites was investigated by fragmentation test. ED results were compared with the dipping and the untreated cases under dry and wet conditions. Multi-fiber composites (MFC) were used for the direct comparison for the untreated and the treated cases. Various treating conditions including time, concentration and temperature were evaluated, respectively. Under dry and wet conditions ED treatment exhibited much higher IFSS improvement compared to the dipping and the untreated cases. Monomeric- and polymeric coupling agents exhibited the comparative IFSS improvement. Adsorption mechanism between coupling agents and carbon fiber was analyzed in terms of the electrolyte molecular interactions during ED process based on to the chain mobility. The microfailure modes occurring from the fiber break, matrix and interlayer cracks were correlated to IFSS.

Introduction

The interfacial shear strength (IFSS) between fiber and matrix is one of the very important factors in characterizing mechanical properties of polymer composite materials. Measuring IFSS between fiber and matrix requires several micro-mechanical techniques. Some of the most frequently used techniques include the single fiber microdroplet test (is called as the single-fiber pullout test),¹⁻³ the fragmentation test (is also called as the single-fiber composites (SFC) test)⁴⁻⁶ and microindentation method⁷ which is usually used in the brittle ceramic matrix composites. Although the SFC test is a difficult testing and analyzing method, it can provide the quantitative information on the interfacial properties such as IFSS value and microfailure modes.⁸⁻¹⁰

IFSS can be improved by introducing chemical functional groups via the oxidation of fiber surface, plasma or commercial coupling agents. Among them, especially ED method¹¹⁻¹³ is a process that a

coating layer is deposited on a conductive surface from a dispersion of colloidal ion in water with a charge opposite to that of the carbon fiber surface. By optimizing the treating process, a polymeric coating may have the desired composition and thickness homogeneously to improve interfacial properties.

A polymeric coupling agent was expected to have better interfacial adhesion compared to a monomeric coupling agent due to its wettability based on polymeric nature. Park⁶ found that there was particularly significant difference in IFSS improvement between monomeric and polymeric silanes. Alkles^{14,15} proposed that, in comparison with monomeric silanes, polymeric silanes could react with substrates more efficiently. The film-forming polymeric silane thus provides a more continuous reactive surface to the polymer matrix in the composite. In comparison with monomeric silanes which carry *trialkoxo* groups, polymeric silanes carrying *dialkoxo* groups can offer superior substrate reactivity and to provide further performance improvements.

In this work, the interfacial properties of the

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untreated, the dipping, and the ED treated carbon fibers/epoxy composites using one monomeric and two polymeric coupling agents were evaluated using fragmentation technique with a microscopic observation. The effect of various surface treatments on the interfacial adhesion was investigated under dry and wet conditions. Adsorption mechanisms on the carbon fiber surface were analyzed in the aspects of the molecular interactions, and microfailure modes were also characterized.

Experimental

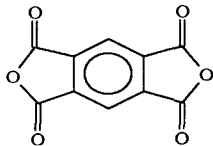
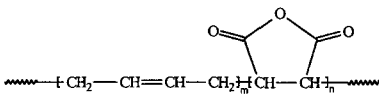
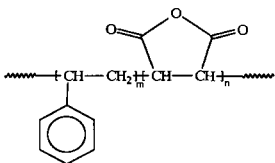
Materials. Carbon fiber was supplied from Tae Kwang Co. (TZ-307). Density and average diameter of the carbon fiber were 1.8 g/cm^3 and $7.9 \mu\text{m}$, respectively. The fiber was subjected to washing with acetone for 10 minutes thoroughly in ultrasonic cleaner to remove any sizing agent or impurities, then dried in air. A diglycidyl ether of bisphenol-A (DGEBA) type epoxy resin (YD-128, Kukdo Chemical Co., Ltd.) was used as the matrix. Polyoxypropylene diamine (Jeffamine D400 and D2000, Huntzman Petroleum Co.) was used as a curing agent. Flexibility of the specimens was controlled by adjusting the relative proportions of D400 versus D2000 in the curing mixture. As

coupling agents, one monomeric pyromellitic dianhydride (PMDA, Aldrich Chemical Co., Inc.) with molecular weight (M.W.) 218 g/mol was used, whereas two polymeric polybutadiene-maleic anhydride (PBMA, Polyscience, Inc.) and polystyrene-maleic anhydride (PSMA, Polyscience, Inc.) with M.W. $10,000\text{--}15,000 \text{ g/mol}$ and M.W. $1,600 \text{ g/mol}$ were used, respectively. PSMA was partially soluble and PMDA and PBMA were completely soluble in the deionized water, and their chemical structures were shown in Table I. Three coupling agents containing same anhydride functional groups were used in order to compare monomeric- and polymeric coupling agents on IFSS.

Methodologies

Fiber Surface Treatments by ED and the Dipping. Main experimental procedures were the ED and the dipping treatments of carbon fibers with coupling agents. First, ED was performed in one compartment cell at room temperature by applying a constant voltage between an aluminum electrode as a cathode and carbon fiber substrate as an anode. About fifty untreated carbon fibers were fixed with regular distance apart individually

Table I. Chemical Structure of One Monomeric and Two Polymeric Coupling Agents

Type	Chemical Name	Chemical Structure	Solvent ^c
Monomeric	Pyromellitic dianhydride (PMDA) ^a		Water (soluble)
	Polybutadiene-maleic anhydride (PBMA) ^b		Water (soluble)
Polymeric	Polystyrene-maleic anhydride (PSMA) ^b		Water (partially soluble)

^aAldrich Chemical Co., Inc.

^bPolyscience, Inc.

^cDeionized and doubly distilled water.

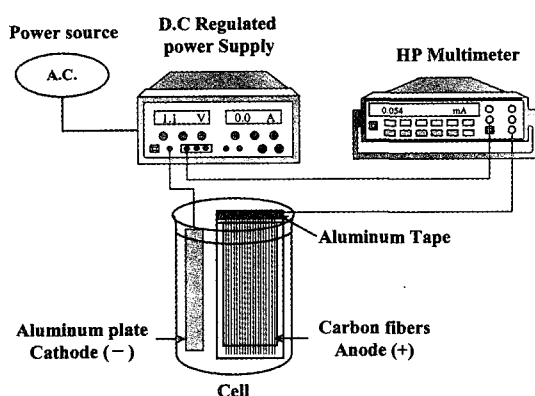


Figure 1. Schematic illustration showing ED system.

in rectangular acrylic frame. This way is to coat uniformly on each fiber surface. The frame with carbon fibers acted as an anode in itself and the cathode was made of an aluminum plate bar with 2 cm in width and 12 cm in length. Silver pastor was also painted to give a good electrical connection. Each coupling agent was diluted to the various concentrations in the deionized water. After the anode frame and the cathode bar were immersed into a certain electrolyte solution, voltage was applied to both electrodes by a conventional DC regulated laboratory power supply (GP 4303TP, LG Electronics) and changing current was recorded using a multi-meter (HP 34401A) as shown in Figure 1. Typical supplying time and applied voltage were 10 minutes and 3 voltages, respectively.

Comparing to ED treatment, the dipping way as a simple conventional surface treatment was performed using the same acrylic frame and electrolyte solution for 2 minutes. After ED and the dipping treatments, carbon fibers were dried at room temperature without further thermal treatment, and some ED treated fibers were dried in the oven in order to compare aging effect at 80°C for 30 minutes.

Adsorption Amount Measurements of Coupling Agents on Carbon Fiber. The surface treatment of carbon fibers by ED or dipping was carried out at various concentrations, temperatures, and treating times, respectively. After the treatment, they were subjected to drying in a vacuum oven for overnight to obtain a constant

weight. Since the extremely tiny weight increased cannot be measured accurately for the individual carbon fiber, total adsorbed weight for the carbon fiber tow with 15 cm in length was measured, then divided into the weight of the initial carbon fiber. The tow on the acrylic frame was gripped tightly using aluminum foil to give the electrical connection. Increased weight ratio and the adsorbed amount per 1 gram of carbon fiber were calculated. The experiment was repeated at least more than three times and the average increased weight was obtained as the adsorbed weight.

Measurements of the Single-Fiber Tensile Strength. Single-fiber tensile testing was carried out by separating the fibers from the tow and individually mounted on each paper frame with various gauge lengths by fixing Scotch tape on both ends, then bonded by using epoxy adhesives. Each diameter of the untreated and the treated carbon fibers was measured individually under an optical microscope attached with calibrated eyepiece lens. The paper frame was then gripped in the Universal Testing Machine (UTM, Lloyd Instruments Ltd.), then both sides in the paper frame were cut carefully with sharp scissors. The tensile test was carried out at a crosshead speed of 1 mm/minute with small capacity 100 N load cell. The tensile strength data were analyzed statistically using Weibull distribution based on weakest-link theory, which the flaw in the material with highest stress intensity factor governs the strength of the material.

Preparation of Multi-Fiber Composite (MFC) Specimens. The dimension of specimens was 3 mm in wide, 25 mm in gauge length, and about 1 mm in thickness, as shown in Figure 2. Four fibers with the untreated and various treated fibers were fixed by using Kaptone (polyimide) tapes on

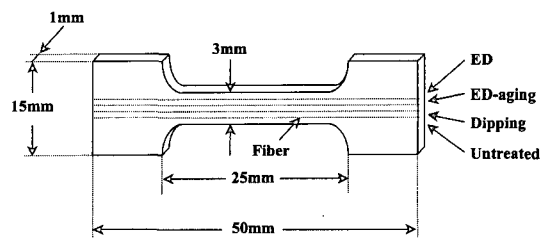


Figure 2. Dimension of dog-bone shaped MFC specimen.

a dogbone shaped silicone mold. They were separated independently with a certain distance apart in a same matrix to avoid the interaction among adjacent fiber. The epoxy resin mixed with Jeffamine curing agents was then poured into silicone mold and stabilized at 50°C for 4 hours to remove air bubble in the mixture. After stabilizing, the specimens were precured at 80°C for 2 hours and then post cured at 120°C for 2 hours. After curing the specimens, the fiber position and its straightness in the specimens were checked via an optical microscope, and then misaligned specimens were discarded. Some specimens from each set were dipped into the aqueous solution on 80°C for 30 minutes to investigate the retention of IFSS under wet condition.

IFSS Measurement. The SFC test method, originally proposed by Kelly-Tyson¹⁶ for fiber/metal composites, can provide abundant statistical information, e.g., the IFSS value and their interfacial failure mechanisms using only a few specimens. The saturated fiber fragment length corresponds to the critical stress transfer length, l_c , which allows the calculation of the apparent shear bond strength at the interface, i.e., IFSS. On the basis of the force balance in a micromechanical model, Kelly-Tyson showed that the IFSS, τ is given by,

$$\tau = \frac{\sigma_f \cdot d}{2 \cdot l_c} \quad (1)$$

Where d is the fiber diameter, σ_f is fiber fracture stress, and l_c is the average critical fragment length. Since a distribution of fragment lengths can be applied, Drzal¹⁷ altered the equation (1) to reflect Weibull distribution as follows:

$$\tau = \frac{\sigma_f}{2 \cdot \alpha} \cdot \Gamma \left[1 - \frac{1}{\beta} \right] \quad (2)$$

Where α is the scale parameter and β is the shape parameter in Weibull distribution for the aspect ratio, and Γ is the Gamma function, respectively.

The MFC test originating from SFC test, and can compare directly the interfacial properties of various multi-fibers embedded in a same matrix, i.e., the untreated or the treated fibers in an identical matrix and testing conditions. The MFC

specimens were tested to obtain IFSS using the mini-tensile tester in which set a hand-turning screw system for stretching the specimen in tensile direction. This unit was mounted on the optical microscope and the MFC specimen was pulled slowly until the fiber break does not occur any more.

In order to know the fiber strength at the critical fragment length, a direct fiber tensile test at such short lengths can result in experimental difficulties. After fiber strengths are usually determined at a measurable short gauge length, they are subjected to subsequent extrapolation to smaller gauge lengths using Weibull weakest-link rule.¹⁸ The tensile strength at a critical fragment length is

$$\frac{\sigma_f}{\sigma_0} = \left(\frac{l_c}{l_0} \right)^{-1/\rho} \quad (3)$$

Where l_0 is the fiber tensile strength at gauge length, l_c and ρ is the shape parameter of Weibull distribution for fiber strength, respectively.

Results and Discussion

Mechanical Properties for Treated Carbon Fibers. The ultimate tensile strength of fiber with brittle fracture behavior depends on the distribution of the defects on the fiber surfaces. The probability of the presence of the defect or the flaw internally and externally in a given fiber length determines the fiber strength. Table II shows the typical mechanical properties for the tensile strength and the elongation of the carbon fiber electrodeposited with PBMA at various gauge lengths. As the gauge length increases, the tensile strength and the elongation decrease, due to randomly distributed defects on fiber surfaces and the heterogeneity between different fibers. Table III shows single fiber tensile strength and elongation of carbon fiber coated with various coupling agents for ED and the dipping methods. Dipping treatments showed the improved tensile strength compared to the untreated and especially than ED treatments. It may be due to the tightly adsorbed coating layer during ED process can damage the fiber surface and act as a stress concentration, in which it can cause the deterioration of the fiber strength. Polymeric coupling agents

Table II. Mechanical Properties of Typical PBMA-ED Treated Carbon Fibers with Various Gauge Lengths

Gauge Length (mm)	No. of Specimens (EA)	Diameter (μm)	Scale Parameter (α)	Shape Parameter (β)	Tensile Strength (MPa)	Elongation (%)
2	46	8.85 (0.15)*	3842	5.41	4458 (721)	6.1 (1.8)
5	48	8.85 (0.16)	3290	5.48	3808 (624)	3.2 (0.6)
10	45	8.85 (0.12)	3024	3.84	3445 (783)	2.1 (0.5)
20	44	8.88 (0.13)	2482	3.95	2841 (616)	1.6 (0.4)
100	45	8.80 (0.21)	2013	4.31	2319 (467)	1.2 (0.3)

*Parentheses are standard deviation.

Table III. Carbon Fiber Tensile Strength with Various Fiber Treatments

Types	No. of Specimens (EA)	Diameter (μm)	Scale Parameter (α)	Shape Parameter (β)	Tensile Strength (MPa)	Improvement (%)	
Untreated	49	7.9 (0.08)*	3097	6.08	2883 (534)	-	
ED	PMDA	50	8.1 (0.08)	3375	5.39	3257 (627)	13.0
	PBMA	44	8.9 (0.31)	2482	3.95	2841 (616)	- 1.5
	PSMA	46	8.1 (0.08)	2182	5.24	2755 (705)	- 4.4
Dipping	PMDA	42	8.0 (0.14)	3439	5.04	3279 (655)	13.7
	PBMA	43	8.2 (0.25)	3433	5.53	3419 (584)	18.6
	PSMA	39	8.2 (0.10)	3255	6.31	3247 (532)	12.6

*Parentheses are standard deviation.

- Gauge length at 20 mm.

showed rather negative improvement for ED method, whereas the dipping treatment showed higher improvement in the tensile strength.

Figure 3 shows SEM photographs of various carbon fiber surfaces. Figure 3(a) shows the untreated clean and neat carbon fiber surface. Figure 3(b) appears lump-shaped PSMA coated layer on the fiber surfaces for 5 minutes coating at higher 0.5 wt% concentration under dipping conditions, whereas Figure 3(c) shows relatively uniform coating layer of PSMA coating for 2 minutes coating at same concentration. On the other hand, Figure 3(d) shows the overall uniform PBMA coated surface compared to the dipping case.

Adsorption Mechanisms on Carbon Fiber Surfaces by ED. ED process is based on the presence in the polymer of ionized groups which render it water dispersible, and which provide the electrical charge to transport when a voltage is applied. The carbon fiber as the substrate to be coated acts as an anodic electrode. Application of an electrical voltage causes the charged polymer particles to migrate to the anode electrode, i.e., carbon fiber surface where they are discharged

and coagulated, thus forming a stable film.

Carbon fibers being electrically conductive can make an ideal substrate in the ED process. By optimizing ED parameters such as concentration, time, and temperature, it should be possible to electrodeposite a coupling agent with desired composition and thickness in which work as a modified interphase, leading to improved mechanical properties. ED on carbon fibers offers a valuable advantage for introducing an interphase in composites: i.e., a complete, uniform coating of the individual fibers can be achieved. As the polymer coating layer is formed, the increased electrical resistance of the coated area induces further film formation to uncoated areas which are more conductive, enabling a film of uniform thickness to be built up, free of pinholes.

In principle, both anodic and cathodic EDs can occur. In anodic ED, the carbon fiber can act as the anode. In cathodic ED, carbon fibers form the cathode. The anode must be inert to prevent the anodic dissolution and the contamination of the bath. Since ED is usually conducted in an aqueous medium, an unavoidable side reaction is the elec-

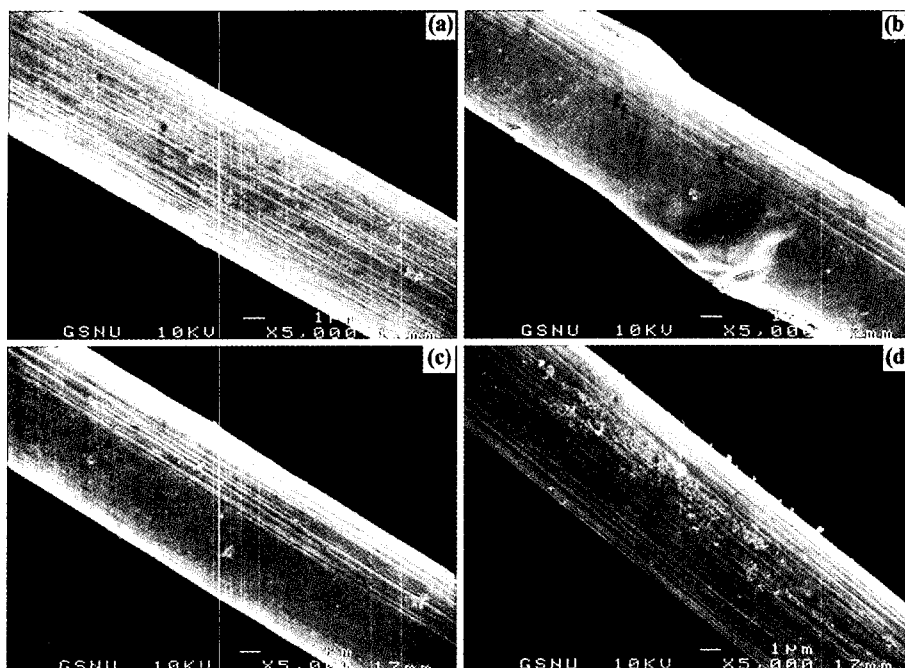


Figure 3. SEM photographs of carbon fibers: (a) the untreated; (b) the dipping carbon fiber (0.5 wt% PSMA, 5 minutes); (c) dipping carbon fiber (0.5 wt% PSMA, 2 minutes); (d) ED treated carbon fiber (0.5 wt% PBMA, 10 minutes).

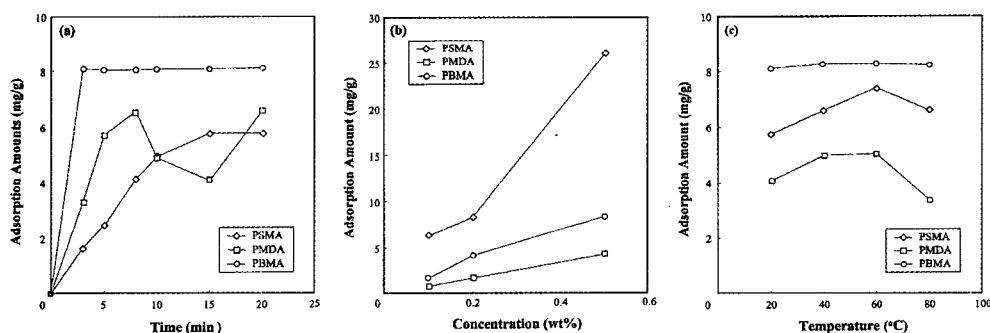


Figure 4. The adsorption amounts of coupling agents on carbon fiber bundle with various experimental conditions: (a) treating time; (b) concentration; (c) treating temperature.

tolysis of water. This results in the evolution of the oxygen at the anode, and twice as much evolution of the hydrogen at the cathode, making the film formed in the latter case more porous. In either method this gassing has to be controlled to prevent desorption the coated layer from the fiber surface.

Figure 4 shows the adsorbed amount of each coupling agent on the carbon fiber bundle depending on various experimental conditions. In

the effect of treating time on 0.5 wt% at room temperature, two polymeric coupling agents, PBMA and PSMA, showed the tendency of saturation in adsorption amount as the treating time increased, whereas a monomeric PMDA coupling agent showed the unstable adsorption behavior as shown in Figure 4(a). This is considered that the adsorbed PMDA molecules may be redissolved into the solution because the dissociation is more dominant than aggregation over a certain

adsorbed thickness and these dissociated molecules may be aggregated again on the carbon fiber surfaces under the influence of the electrical attraction after dissociation. In the effect of the concentration in Figure 4(b), adsorbed amounts of three coupling agents at room temperature for 10 minutes increased as the concentration increased. It is considered that there can be higher probability to be adsorbed on the carbon fiber surfaces due to the larger molecules of dissolved coupling agent and the higher concentration in the aqueous solution. In case of PSMA, adsorption amounts exhibited significant high value since PSMA was dissolved completely with NaOH solution to become a salt state unlike Figure 4(a) case.

In the effect of temperature in Figure 4(c), adsorption amounts of two coupling agents, PSMA and PMDA, at 0.5 wt% solution for 10 minutes had the maximum values at 60°C as temperature increased, then decreased. It is considered because PSMA and PMDA with having comparatively low molecular weight can be adsorbed dominantly due to high chain mobility as the treating temperature increased, whereas the dissociation of adsorbed molecules also occur dominantly above the critical temperature. In case of PBMA having relatively low chain mobility due to high M.W., it exhibited the trend to be independent of treating

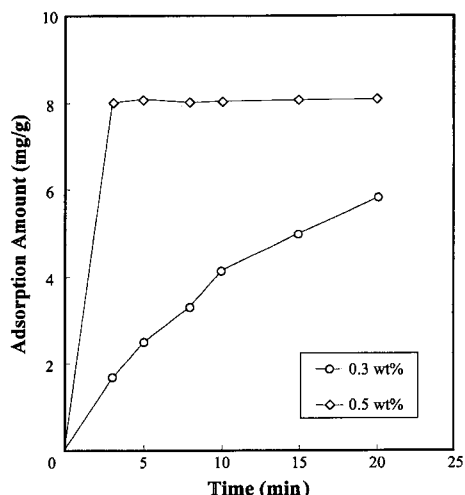


Figure 5. Treating time versus the adsorption amount of PBMA on carbon fiber bundle according to concentration at room temperature.

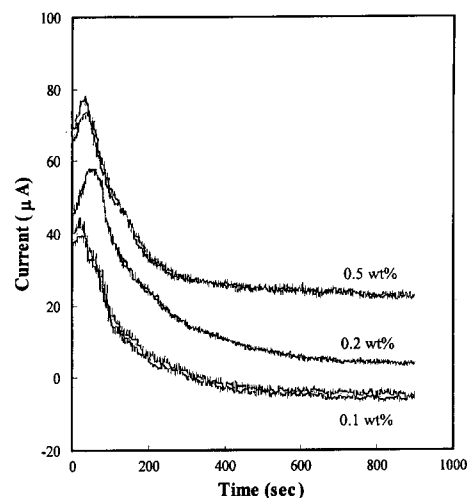


Figure 6. Current changes during ED depending on PMDA concentration.

temperature.

Figure 5 shows the adsorption amount of PBMA in carbon fiber bundle depending on the treating time according to the concentration at room temperature. The case of 0.5 wt% concentration did not show the changes of the adsorption amount depending on the treating time, while the adsorption amount at 0.3 wt% concentration increased as the treating time increased and can be expected to saturate eventually.

Figure 6 shows current changes during ED process depending on PMDA concentration. It was observed that the higher the measured current was, the higher the concentration was. Because the high concentration of electrolytes can be dissolved in the aqueous solution, the current exhibited high value comparatively. Current increases initially up to 20-30 seconds then decreases. Positively charged carbon fiber can attract the negative charged carboxylate ion in the solution. It is because it the electrolytes can move rapidly to the carbon fiber surfaces initially, then the concentration of the electrolytes in the aqueous solution decreased with an increase of the adsorbed layer.

Figure 7 shows schematic mechanisms of the adsorption and the desorption between carbon fiber surfaces and dissolved polymeric coupling agents. Equilibrium state between the adsorption and the desorption may occur. Excess adsorbed

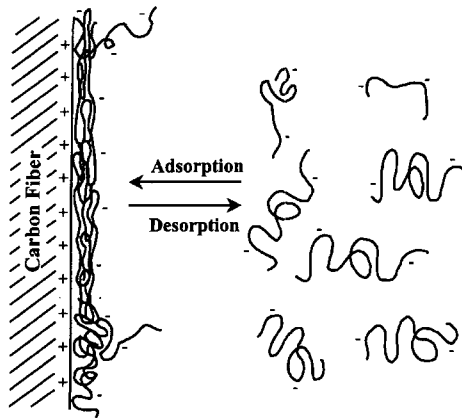


Figure 7. Mechanism of adsorption and desorption between carbon fiber surface and dissolved polymeric coupling agent.

coupling agents may be dissolved again especially at high temperature condition as described previously in Figure 4(c). During ED process the adsorption can occur in terms of the electrical attraction by the polarization in aqueous solution. On the other hand, after ED processing, electrical attraction force disappears and the primary and the secondary force may work in the interphase between carbon fiber and adsorbed coupling agent.

IFSS of Carbon Fibers/Epoxy Composites on Surface Treatments. Table IV and Figure 8 show the data for IFSS of carbon fiber/epoxy composites on treating methods of coupling agents.

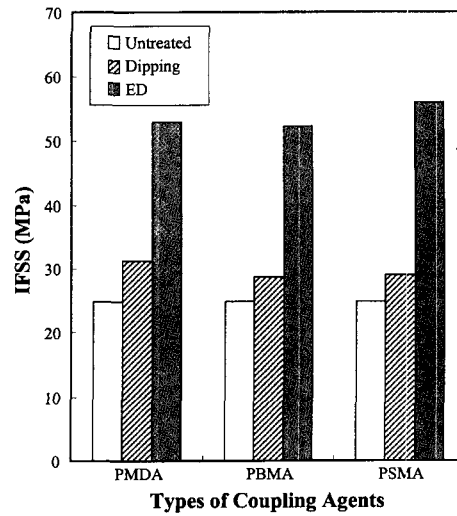


Figure 8. Comparison of IFSS depending on treatment types of various coupling agents in carbon fiber/epoxy composites.

As shown in Table IV, it was identified that average fragment length and aspect ratio, l/d , were the largest in the untreated case and the smallest in the ED treatment. Fiber tensile strength at critical fragment length, l_c , was obtained by applying Weibull weakest-link rule. Scale and shape parameters were obtained from Weibull distribution for the aspect ratio. IFSS of carbon fiber/epoxy composites showed the highest value at the ED treatment compared to the dipping and the untreated cases. Polymeric coupling agents did not

Table IV. Interfacial Parameters Depending on Treating Methods and Three Coupling Agents

Types	Average Fragment Length (μm)	Aspect Ratio (l/d)	Fiber Strength (MPa) ^a	Scale Parameter (α) ^b	Shape Parameter (β) ^b	IFSS (MPa)		
						Drzal ^c	Kelly-Tyson ^d	
Untreated	620	78.5 (21.7)*	3487	86.8	3.92	24.9	22.2	
Dipping	PMDA	579	73.3 (18.6)	4193	80.5	4.33	31.3	28.6
	PBMA	634	80.2 (19.8)	4209	87.5	4.53	28.6	26.2
	PSMA	588	74.4 (18.5)	3944	81.6	4.39	29.0	26.6
ED	PMDA	359	45.5 (10.4)	4479	49.5	4.99	52.8	47.9
	PBMA	366	46.3 (13.4)	4376	51.2	3.86	52.1	47.9
	PSMA	337	42.7 (13.9)	4172	47.5	3.56	55.9	48.8

*Parentheses are standard deviation.

^aFiber tensile strength at l_c using Weibull weakest link rule.

^bValue for aspect ratio.

^cDrzal equation : $\tau = (\sigma_f/2\alpha) \cdot I(1-1/\beta)$.

^dKelly-Tyson equation: $\tau = (\sigma_f \cdot d)/(2 \cdot l_c)$.

Table V. Interfacial Parameters as a Function of Various Surface Treatments Using PBMA Coupling Agent under Dry and Wet Conditions

Types		Average Fragment Length (μm)	Aspect Ratio (l_c/d)	Fiber Strength (MPa) ^a	Scale Parameter (α) ^b	Shape Parameter (β) ^b	IFSS (MPa)	
							Drzal ^c	Kelly-Tyson ^d
Dry	Untreated	620	78.5 (21.7)*	3487	86.8	3.92	24.9	22.2
	Dipping	634	80.2 (19.8)	4209	87.5	4.53	28.6	26.2
	ED	366	46.3 (13.4)	4376	51.2	3.86	52.1	46.2
	ED-aging	461	58.3 (14.2)	4127	63.9	4.50	38.5	35.4
Wet ^e	Untreated	688	87.1 (24.7)	3429	96.3	3.89	21.5	19.6
	Dipping	710	89.9 (24.1)	4123	99.9	3.81	25.4	22.8
	ED	413	52.2 (16.9)	4244	58.1	3.42	46.4	41.1
	ED-aging	496	62.8 (19.8)	4091	69.9	3.54	37.5	32.3

*Parentheses are standard deviation.

^aFiber tensile strength at l_c using Weibull weakest link rule.

^bValues for aspect ratio.

^cDrzal equation: $\tau = (\sigma_f/2\alpha) \cdot \Gamma(1-1/\beta)$.

^dKelly-Tyson equation: $\tau = (\sigma_f \cdot d)/(2 \cdot l_c)$.

^eWet condition : 30 minutes at 80 °C.

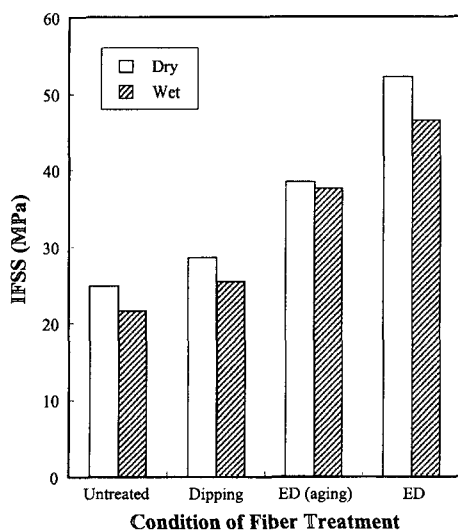


Figure 9. Comparison of IFSS depending on various surface treatment method under dry and wet conditions.

show the remarkable difference in IFSS compared to monomeric coupling agent in Figure 8.

Table V shows the aspect ratio and IFSS under dry and wet conditions depending on various type carbon fibers using PBMA coupling agent. Average fragment length and aspect ratio under wet condition were higher compared to dry condition. ED treatment also showed the highest IFSS value. Figure 9 exhibits the IFSS comparison

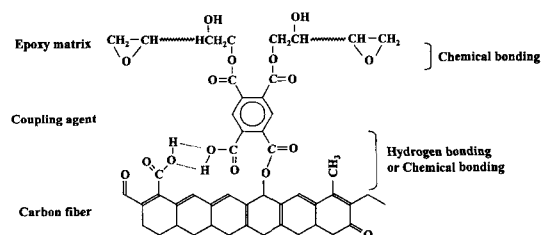
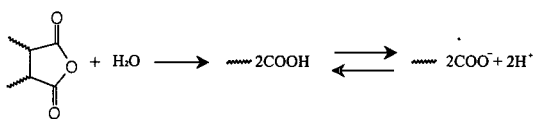


Figure 10. Schematic illustration showing possible chemical reaction among the carbon fiber/coupling agent/epoxy system.

of four carbon fibers/epoxy composites under dry and wet conditions for different fiber surface treatments. The IFSS values of ED treatment indicate the retention of adhesive bonding between fiber and matrix under wet environment. ED-aging case exhibited rather lower IFSS value.

Figure 10 shows a schematic model of possible bonding mechanisms among carbon fiber, monomeric PMDA coupling agent and epoxy matrix. As the first interphase there can be the secondary hydrogen bonding and the primary chemical bonding between carbon fiber surface and PMDA coupling agent. On the other hand, as the second interphase the chemical bonding and interdiffusion between PMDA coupling agent and epoxy matrix may contribute to improve the interfacial adhesion.



Anhydride groups attached in both monomeric- and polymeric coupling agents can be hydrolyzed in aqueous solution to offer carboxylic group, in which can react with minor functional group in the carbon fiber surface, such as ether, hydroxyl, and carboxyl groups etc. With a carboxylate function after ring anhydride opening reaction in the aqueous solution, the anodic oxidation may result in the crosslinking of the polymer, or the grafting of the resin onto the carbon fiber. These result in the improved interfacial adhesion, and

then enhanced the mechanical performance in composite materials. It may be also important to know how the epoxy resin mixed with curing agents reacts with the coupling agent-treated carbon fiber. The reorientation of coupling agent molecules at the carbon fiber can occur against the epoxy resin.

Typical failure modes without and with polarized-light were shown for various treating conditions in carbon fiber/epoxy composites at 4% strain in Figure 11. In the untreated case (a), only debonding was observed after carbon fiber breakage. In the dipping case (b) the interlayer failure was accompanied immediately after fiber breakage, then debonding length became larger as the strain

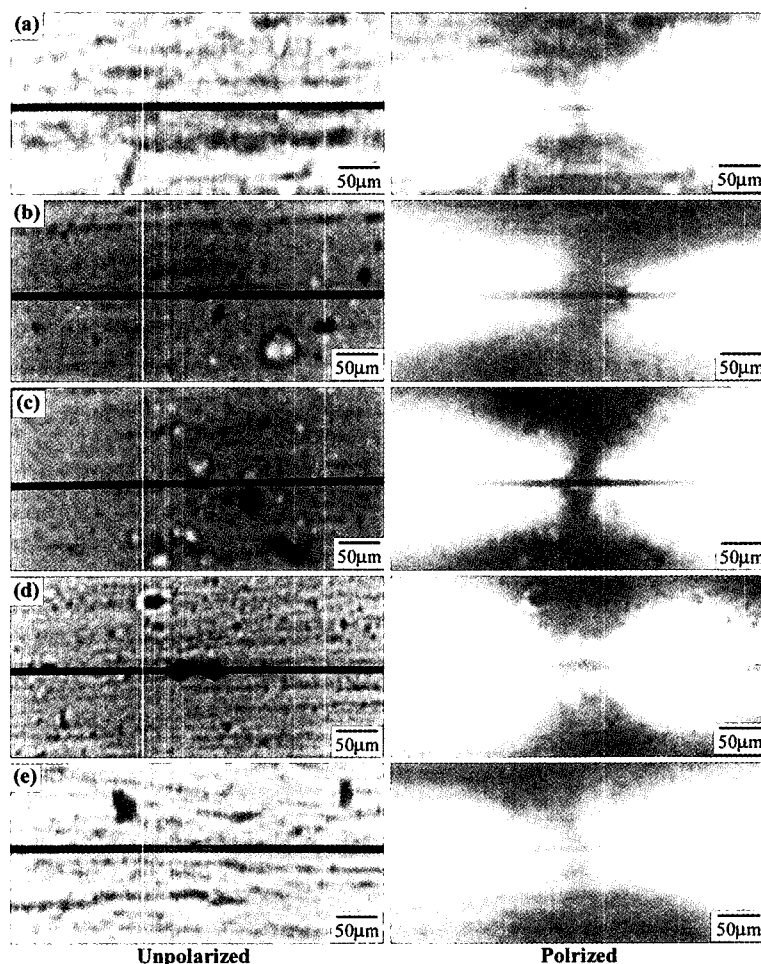


Figure 11. Typical failure modes for various treating conditions in carbon fiber/epoxy composites: (a) the untreated; (b) the dipping; (c) aging after ED; (d) ED; (e) all fibers under wet conditions.

Comparison of Electrodeposited Carbon Fibers Reinforced Epoxy Composites

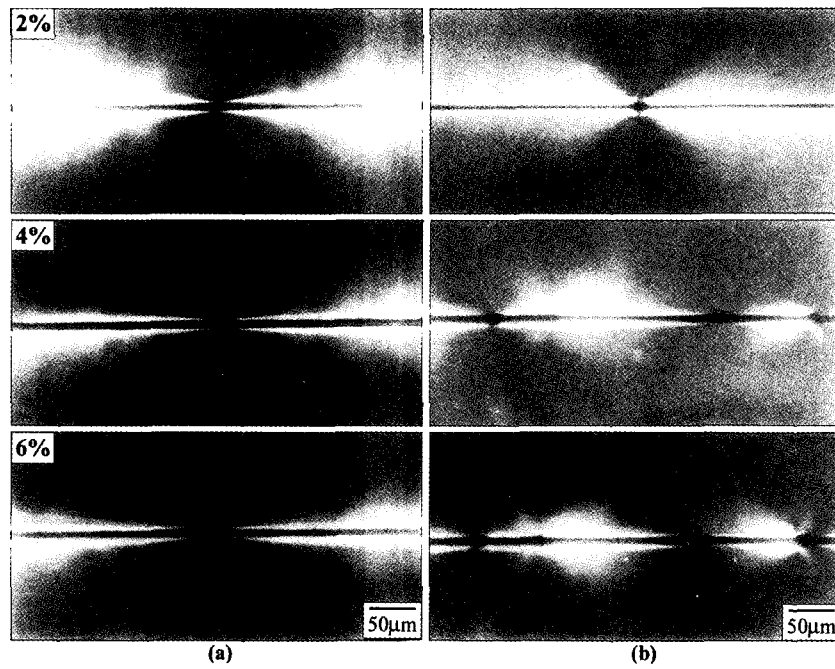


Figure 12. Polarized-optical photographs of single carbon fiber/epoxy composites on strain increase: (a) the untreated; (b) ED.

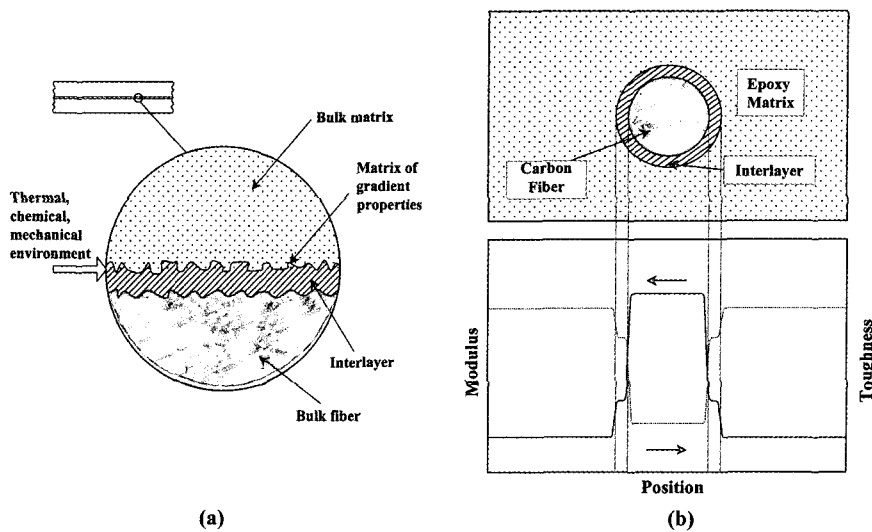


Figure 13. Schematic illustrations showing (a) the longitudinal shape of the two dimensional interphase between fiber and matrix; (b) the cross sectional region of the modulus and toughness of the components on the position.

increased. In the ED-aging case (c) the diamond shape failure was shown at initial state as the ED case (d), but the debonding length become larger as the strain increased like the dipping case. After stayed under sufficient wet condition (e), all fibers

appeared only the debonding phenomena.

Figure 12 shows photographs using polarized-light microscopy of single carbon fiber/epoxy composites with increasing strain for (a) the untreated and (b) ED. More fiber fractures were

observed in ED case with increasing strain, since the stress can be transferred much more to carbon fiber in ED case compared to the untreated case.

Figure 13 shows schematic illustrations showing (a) the longitudinal shape of two-dimensional interphases between fiber and matrix; and (b) the cross sectional region of the modulus and toughness of the components on the position in SFC system. In Figure 13(a), matrix gradient properties can occur due to interdiffusion between coupling agent layer and epoxy matrix, whereas more like chemical reaction can exist between fiber surface and coupling agent. In figure 13(b), there may be two-transitional interphase regions on modulus and toughness among carbon fiber, interlayer, and epoxy matrix. Thermal, chemical, and mechanical environment may affect on the interfacial properties relating with mechanical properties directly.

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Conclusions

The interfacial properties on various surface treatments for carbon fiber/epoxy composites were obtained by means of multi-fiber fragmentation tests with an optical microscopic observation. ED treatment exhibited much higher IFSS improvement compared to the dipping and the untreated cases. Polymeric coupling agents did not show remarkable difference in IFSS compared to a monomeric coupling agent. The optimum conditions were obtained from the comparison of adsorption amounts of coupling agents with various treating times, concentrations and temperatures. Adsorption mechanisms on the carbon fiber surface were explained in term of the chain mobility due to the different molecular weight.

IFSS and their microfailure modes are correlated to each other under dry and wet conditions. The different number of fiber fragmentation occurring from the different interlayer can result in the differing interfacial properties to affect the final IFSS. This is because of the different role of the different interlayer based on the mechanical and chemical properties, respectively.

References

- (1) T. Grubb and Z. F. Li, *J. Mater. Sci.*, **29**, 189 (1994).
- (2) A. R. Sanadi and M. R. Piggott, *J. Mater. Sci.*, **20**, 431 (1985).
- (3) M. H. Auvray, P. Cheneau-Henry, F. H. Leroy, and J. P. Favre, *Composites*, **25**, 776 (1994).
- (4) J. M. Park, R. V. Subramanian, and A. E. Bayoumi, *J. Adhesion Sci. & Technol.*, **8**, 133 (1994).
- (5) J. M. Park, J. O. Lee, and T. W. Park, *Polym. Compos.*, **17**, 375 (1996).
- (6) J. M. Park and R. V. Subramanian, *J. of Adhesion Sci. & Technol.*, **5**, 459 (1991).
- (7) D. B. Marshall and W. C. Oliver, *Mater. Sci. & Eng.*, **A126**, 95 (1990).
- (8) J. M. Park, E. M. Chong, D. J. Yoon, and J. H. Lee, *Polym. Compos.*, **19**, 747 (1998).
- (9) S. I. Lee, J. M. Park, D. W. Shin, and D. J. Yoon, *Polym. Compos.*, **20**, 19 (1999).
- (10) J. M. Park, J. W. Kim, and K. Goda, *Compos. Sci. & Technol.*, **60**, 439 (2000).
- (11) R. V. Subramanian and A. S. Crasto, *Polym. Compos.*, **7**, 201 (1986).
- (12) R. A. Wessling, in *Electrodeposition of Coatings*, R. F. Gould Ed., Advances in Chemistry Series 119, Am. Chem. Soc., 110 (1973).
- (13) K. Kim and H. J. Yoo, *Surf. Coatings & Technol.*, **108**, 564 (1998).
- (14) B. Arkles, J. Steinmetz, and J. Hogan, *SPI Reinforced Plastics/Composites Annual Tech. Conf.*, **42**, 21-C (1987).
- (15) B. Arkles, J. Steinmetz, and J. Hogan, *Mod. Plast.*, May, 138 (1987).
- (16) A. Kelly and W. R. Tyson, *Mech. Phys. of Sol.*, **13**, 329 (1965).
- (17) L. T. Drzal, M. J. Rich, M. F. Koenig, and P. F. Lloyd, *J. Adhesion*, **16**, 133 (1983).
- (18) W. A. Curtin, A. N. Netravai, and J. M. Park, *J. Mater. Sci.*, **29**, 4718 (1994).