

Effect of Polyamic Acids on Interfacial Shear Strength in Carbon Fiber/Aromatic Thermoplastics

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Synopsis

Carbon fiber surfaces were coated in various thickness with polyamic acids (PAA) prepared from (1) benzophenone tetracarboxylic dianhydride (BTDA) and 4,4'-diaminodiphenyl ether (ODA), (2) BTDA and 4,4'-diaminodiphenyl sulfone (DAS), and (3) BTDA and ODA modified with bisaminopropylsilane, designated as PAA-1, PAA-2 and PAA-3 respectively. The treated carbon fiber, with or without imidization, was embedded in thermoplastic polyetheretherketone (PEEK), polyetherimide (PEI), polyethersulfone (PES), polysulfone (PSF), and polyphenylsulfide (PPS) by the microbond method, and the interfacial shear strength was measured by pulling out the fiber from the embedded resin. Maximum increments in interfacial bonding strength from 24% to 35% were obtained from PAA-1 in PEEK and PEI, PAA-2 in PEEK, PEI, PSF, and PPS, and PAA-3 in PEEK and PES. Imidization of PAA-1 and PAA-2 before resin application reduced their bonding capability. A linear relationship between the length of the embedded fiber and debonding load was found in the case of PEEK, PEI, and PSF; scattered results were obtained in the case of PES and PPS. Inadequate specimen annealing was believed to be the cause for PES, Brittle fracture appeared to occur in the case of PPS.

INTRODUCTION

Interfacial bonding agents are commonly used in composite materials for improving interfacial bonding, e.g., silanes used in glass fiber reinforced plastics. To date, most of the composite materials are based on thermosetting resins for their thermal and dimensional stabilities. In recent years heat resistant thermoplastics rich in aromatic content have emerged. The development of composites based on these thermoplastics reinforced with carbon/graphite fiber is the goal for plastic materials of superior performance.¹

Carbon fibers have low surface energy. They require special surface treatment such as chemical oxidation, plasma etching, etc. for interfacial bonding.² In conjunction with the surface treatment, interfacial bonding agents are also applied to the fibers used in matrix resins like epoxies, unsaturated polyesters, etc. These bonding agents, including epoxy, phenolic, furfuryl resins, polyvinyl alcohol and others,²⁻⁵ can hardly withstand the processing temperature

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(> 350°C) for these high performance thermoplastics. Therefore, heat resistant bonding agents must be developed for composite materials derived from these thermoplastic resins.

Polyimides have good thermal stability. They are being used as high temperature adhesives. Their application as heat resistant interfacial bonding agents appear to be attractive. Kodama et al.⁶ used polyimide coated carbon fibers in epoxy laminates and obtained improvement in tensile and T-peel strength. On the other hand, Marks et al.³ did not find any improvement in flexural test for polyimide coated graphite fiber in epoxy resins.

In this article, we used polyamic acid treated carbon fibers, with or without imidization, embedded in PEEK, PEI, PES, PSF, and PPS by the microbond method, and measured the interfacial shear strength by pulling out the fiber from the embedded resin.

EXPERIMENTAL

The materials used in the experiments are as follows. Carbon fiber: Hysol/Grafil type X/H-S 12K, unsized. Thermoplastic resins: PPS (Polyphenyl sulfide), Toray, Japan, PEEK (Polyetheretherketone), ICI, England, PEI (Polyetherimide); Westlake, U.S.A., PES (Polyethersulfone), Westlake, U.S.A., PSF (Polysulfone), Westlake, U.S.A. Chemical reagents: BTDA (3,3',4,4'-benzophenone tetracarboxylic dianhydride), Polysciences Inc., ODA (4,4'-diamino-diphenyl ether), Merck-Schuchardt, DAS (4,4'-diamino-diphenyl sulfone), Merck-Schuchardt, APMS (1,3-bis(γ -aminopropyl) tetramethyl disilane), Silar.

Preparation of Polyamic Acids, PAAs

BTDA, ODA, and DAS were purified by sublimation under reduced pressure. The solvents used were dried over P₂O₅, then distilled.

PAA-1 (BTDA/ODA)

Powdered BTDA (16.1 g., 0.05 moles) was added in several portions to a solution of ODA (10.0 g., 0.05 moles) in 150 mL of DMF with stirring under N₂. The reaction proceeded for 4 h. at room temperature. The solid content of the solution was approximately 15% by weight.

PAA-2 (BTDA/DAS)

PAA-2 was prepared under the same conditions as above from equimolar BTDA and DAS in DMF solution.

PAA-3 (BTDA/ODA/APMS)

PAA-3 was prepared from equimolar BTDA and diamines in NMP solution. The diamines contained ODA and APMS in a molar ratio of 9 : 1.

The inherent viscosity of the PAAs was measured in the solvent used at a concentration of 0.5 g/dL and a temperature of 25°C with a Cannon-Ubbelohde K100 viscometer.

TABLE I
The Thermal and Mechanical Properties of Thermoplastic Resins

Property	PES ¹¹	PEI ¹⁰	PSF ⁹	PEEK ¹¹	PPS ⁹
Tensile strength, (kg/cm ²)	845	1070	704	1021	669
Elongation, (%)	40–80	50–100	60	> 100	3
T_m (°C)	—	—	—	334	285
T_g (°C)	230	217	190	145	89

Surface Treatment of Carbon Fibers

Carbon fibers were cut approximately 30 cm in length, washed with acetone, then dried.

A weighed sample of carbon fiber was immersed in a solution containing 1–5% of PAA by weight. The sample was drip dried, then heated to 80°C in a vacuum oven to a constant weight. The amount of PAA added on the fibers was calculated from weight increment.

Imidization of PAA

A portion of the treated carbon fiber was heated at 300°C for 1 h to convert the polyamic acid into polyimide. The samples were designated as PI-1, PI-2, and PI-3 from PAA-1, PAA-3, and PAA-3, respectively.

Microbonding Resin to Carbon Fiber

A single filament of carbon fiber was mounted on a U-shaped aluminum frame. The resin to be coated was heated to melt, and a droplet of the molten resin was applied to the carbon fiber from a needle point. This operation was carried out under a stereomicroscope. The prepared samples were annealed at 240°C for 2 h, then cooled gradually to room temperature. The length of carbon fiber embedded in resin was measured with a micrometer under the microscope; and one end of the carbon fiber was cut flush to the embedded resin droplet.

Debonding Test

The prepared specimen was clamped to a Shimadzu AGS 100 testing machine equipped with a load cell of 100 g. The force required to pull out the fiber

TABLE II
The Composition and Inherent Viscosity of Polyamic Acids

Sample	Composition (mole ratio)	η_{inh} (dL/g)
PAA-1	BTDA/ODA (1 : 1)	0.97
PAA-2	BTDA/DAS (1 : 1)	0.85
PAA-3	BTDA/ODA/APMS (1 : 0.9 : 0.1)	0.94

TABLE III
Percent of PAAs and PIs Added on Carbon Fiber

Sample	Add-on (% fiber)			
	1	2	3	4
PAA-1 & PI-1	1.5	2.6	4.0	5.8
PAA-2 & PI-2	1.0	2.0	4.3	5.4
PAA-3 & PI-3	1.2	2.0	4.3	—

from the embedded resin was recorded at a crosshead displacement speed of 0.5 mm/min.

RESULTS AND DISCUSSION

Description of Materials

The carbon fiber used in our experiments was Hysol/Grafil type X/H-S, unsized. Manufacturer's specifications are as follows:

Specific gravity, g/cm ³	1.8
Tensile strength, 10 ³ kg/cm ²	37.7
Tensile modulus, 10 ⁶ kg/cm ²	2.3–2.5
Elongation, %	1.5–1.7
Fiber diameter, μm	6.6

The thermal and mechanical properties of the thermoplastic resins are listed in Table I; and the chemical composition and inherent viscosity of the polyamic acids prepared are given in Table II.

Preparation of Testing Specimen

Carbon fibers were surface treated with PAAs by immersion in a solution of PAA at concentrations ranging from 1 to 5% in DMF or NMP (cf experimental). The dry weight of PAAs added onto the fibers are given in Table III.

A portion of the PAA treated fiber was imidized at 300°C. The amount of polyimide added on was taken to be the same as the PAA. At 1% of add-on, the thickness of coating was about 7 nm.

The treated fiber was embedded in resin by the microbond method. Miller et al.⁷ have shown that this method gives fairly reproducible results in the case of epoxy resin. The prepared specimens were annealed at 240°C for 2 h.

Interfacial Shear Strength

The force required to pull out the carbon fiber from the embedded resin was recorded by a Shimadzu AGS 100 testing machine equipped with a load cell of 100 g. The machine was calibrated with standard weights in the range of 0–10 g. A sketch of the sample assembly is shown in Figure 1.

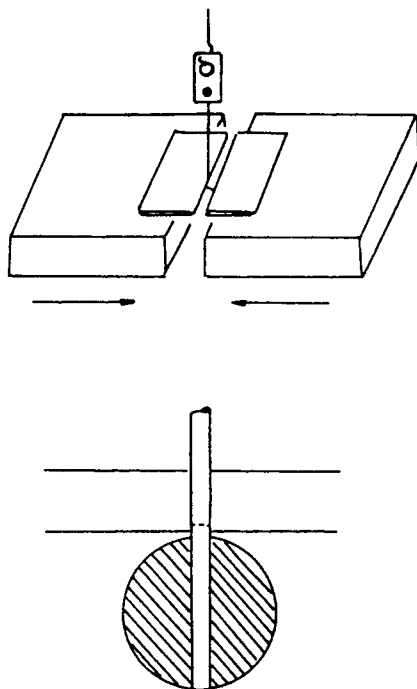


Fig. 1. Arrangement for shear debonding (top) and enlarged resin droplet on a fiber under the shearing plates (bottom).⁷

The interfacial bond strength was equated to the maximum interfacial shear stress, derived from the measured pull-out force, by the following relationship.

$$\tau = \frac{f}{\pi \cdot d \cdot l}$$

Where τ is the maximum shear stress, f is the measured pull-out force, d is the diameter of carbon fiber, and l is the length of carbon fiber embedded in resin.

TABLE IV
Interfacial Shear Strength between Carbon Fiber and Matrix Resins

Matrix resin	Interfacial bond strength (kg/cm ²)	
	With annealing ^a	Without annealing
PES	324 ± 59	282 ± 7
PEI	359 ± 34	141 ± 14
PSF	345 ± 34	21 ± 3
PEEK	380 ± 30	25 ± 2
PPS	275 ± 39	71 ± 14

^a Annealed at 240°C for 2 h.

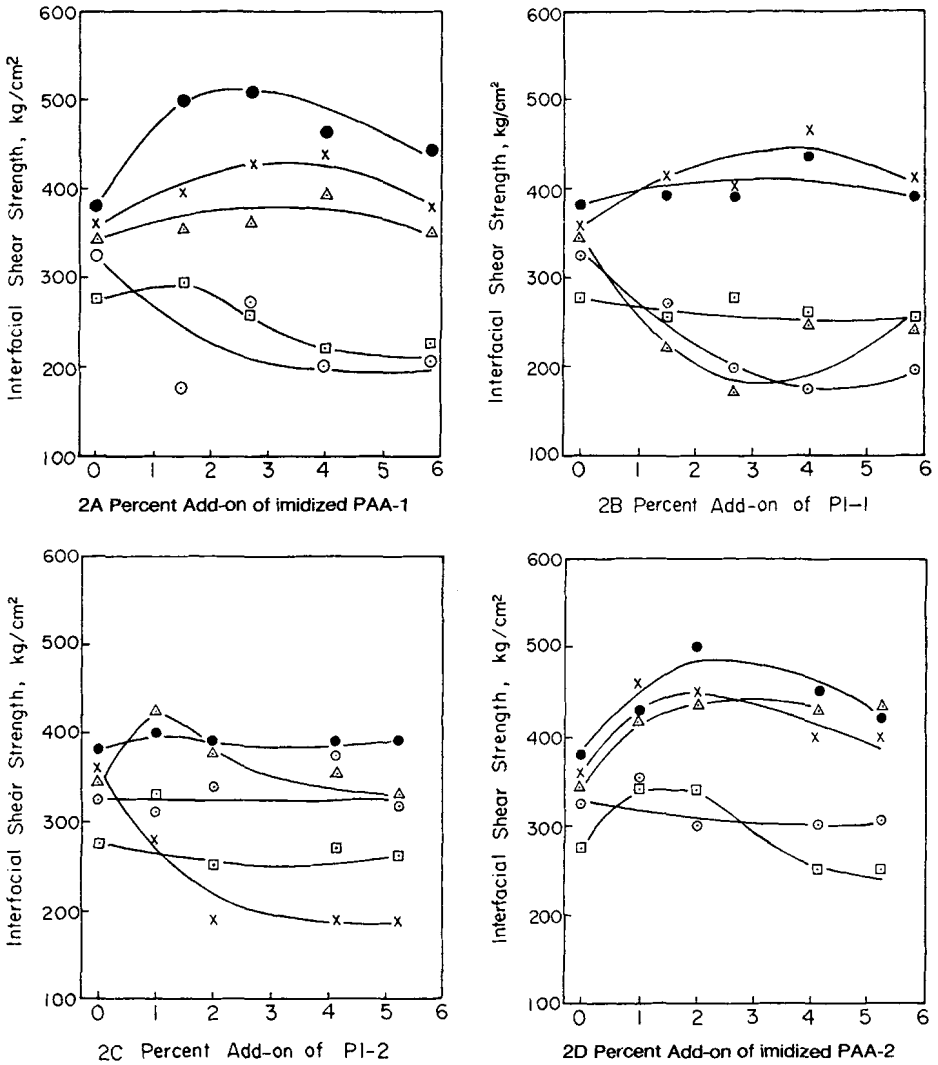


Fig. 2. Interfacial shear strength between carbon fiber and thermoplastics: (●) for PEEK, (×) for PEI, (Δ) for PSF, (○) for PES, and (□) for PPS.

Table IV gives the results obtained from untreated carbon fiber embedded in the various thermoplastic resins with or without annealing. The results showed explicitly that annealing was a necessary step for promoting interfacial bonding. At least five specimens were tested for each sample. The variations were $\pm 18\%$ for PES and $\pm 14\%$ for PPS, while the remaining resins showed variations within $\pm 10\%$.

The results obtained from carbon fibers coated with different PAAs or PIs at various thickness, and embedded in different thermoplastic resins are plotted in Figure 2. As shown in Figure 2(A), PAA-1 showed a positive effect on interfacial bonding in PEEK and PEI. The maximum increment in interfacial bond strength was 35% and 26%, respectively, obtained at a PAA add-on of about 3%. No improvement in interfacial bonding was obtained in PSF, and

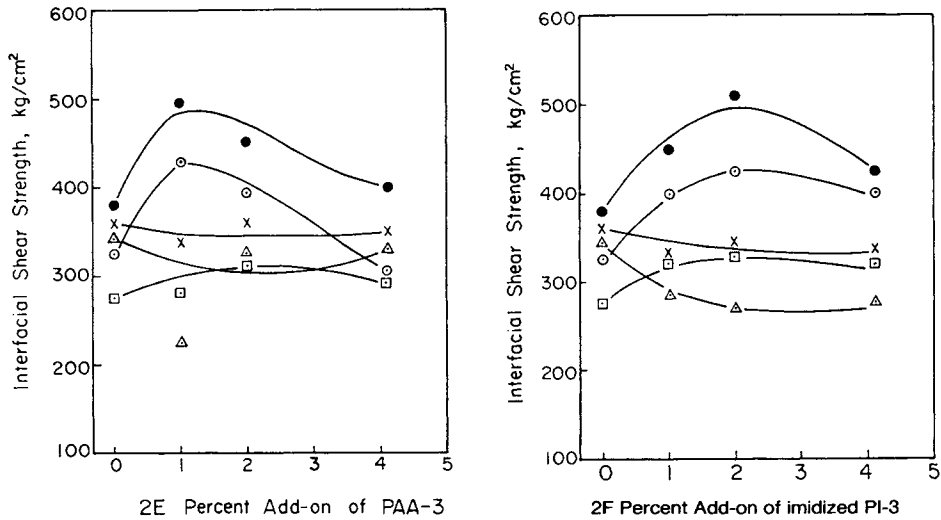


Fig. 2. (Continued from the previous page.)

adverse effect was observed in PES and PPS. Although polyamic acids can be imidized to a large extent at the annealing temperature, imidization of PAA-1 before resin application reduced its bonding capability as shown from the results given in Figure 2(B).

PAA-2 gave improved interfacial bonding with the thermoplastic resins, except PES. The maximum increment in bonding strength was 35% for PEEK, 28% for PEI, 26% for PSF, and 24% for PPS at an optimal add-on of 2% (Fig. 2(C)). Imidization of PAA-2 before resin application also reduced its bonding capability (Fig. 2(D)).

PAA-3 was a modified PAA-1 with increased flexibility. It showed positive results in PEEK and PES with increases in bonding strength of 32% and 28% respectively, at an optimal add-on of about 1% (Fig. 2(E)). Imidization of PAA-3 before resin application did not affect its bonding capability. On the contrary, it gave better results in PPS (Fig. 2(F)).

TABLE V
Effect of Bonding Agents on Interfacial Shear Strength between
Carbon Fiber and Matrix Resin^a

Resin	Bonding agent					
	PAA-1	PI-1	PAA-2	PI-2	PAA-3	PI-3
PEI	+	+	+	-	0	0
PSF	0	-	+	+	-	-
PEEK	+	0	+	0	+	+
PES	-	-	0	+	+	+
PPS	0	0	+	0	0	+

^a + denotes an increase in ISS by 15% or more, - denotes a decrease in ISS by 15% or more, 0 denotes variations within $\pm 15\%$.

The above results are summarized in Table V, where the symbols “+” and “-” denote respectively an increase or a decrease in interfacial bond strength by 15% or more, and “0” denotes variations within the confidence limits of approximately $\pm 15\%$.

In a comparison between the various PAAs, PAA-2 seemed to be more versatile as a bonding agent than the others for these thermoplastic resins with the exception of PES. Its chemical structure has some resemblance to both PSF and PES. The improved interfacial bonding obtained from PSF may be attributed to a better chemical affinity between them, since both PAA-1 and PAA-3 showed negative results in PSF. The poor experimental results obtained from PES could be a consequence of its high T_g (230°C) as compared to the annealing temperature (240°C). Apparently, the PES specimens were not properly annealed.

Among the various thermoplastic resins, PEEK gave the best results in interfacial bonding with the various PAA treated carbon fibers. This polymer has an elongation of $> 100\%$ at break. Its pliable polymer chains could make better interfacial contact with the fiber surface, and result in stronger bonding strength. In fact, this polymer also gave the highest interfacial shear strength with untreated carbon fiber; while PPS, the most rigid polymer among these resins, gave the lowest value.

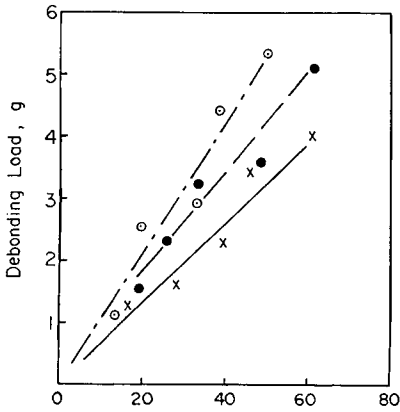
Imidization of PAA-1 and PAA-2 yielded less flexible PIs which gave poor interfacial bonding as compared to their respective PAAs. On the other hand, PAA-3 and PI-3, both appeared to be sufficiently flexible and gave comparable results in bonding strength. Therefore, interfacial bonding depended not only on the chemical affinity between the bonding agent and the polymeric substrate, but also on the physical properties of both.

Reliability Test

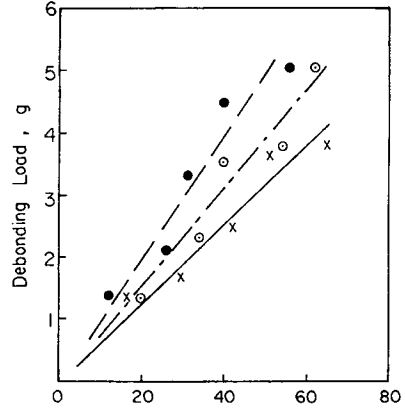
From the fiber diameter and the ultimate tensile strength, a single filament of carbon fiber can sustain a load of 12.9 g. So long as the interfacial shear strength does not exceed this value, the fiber can be pulled out from the embedded resin. The pull-out force, f , should be proportional to the embedded length, l .

However, from a study of carbon fiber reinforced epoxy resins, Piggott⁸ has shown that the relationship between f and l is depended upon the fracture mechanism. A linear relationship is obtained only under the condition where the composite fails by shear yield at the interface. The pull-out force f tends to level off at higher values of l , and large variations in testing results may be observed from composites which fail by brittle fracture. In extreme cases, f becomes independent of l in composites with low shrinkage stress, where good interfacial bonding is not achieved. In the latter cases, reliable performance of the composite materials can hardly be expected. Thus, a test of this function would show the reliability of our experimental results.

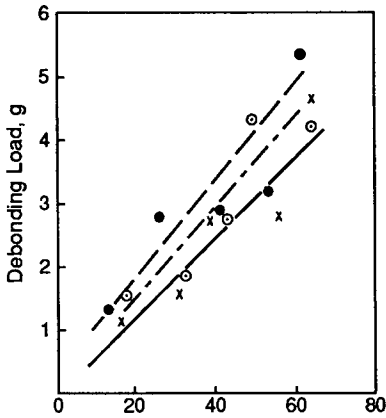
Figure 3(A) shows the results obtained from carbon fiber with and without PAA treatment embedded in PEEK. A good linear relationship between f and l existed in all cases. Similar results were obtained from PEI (Fig. 3(B)). The results showed larger variations in the case of PSF (Fig. 3(C)), and became more scattered in the case of PES (Fig. 3(D)) and PPS (Fig. 3(E)).



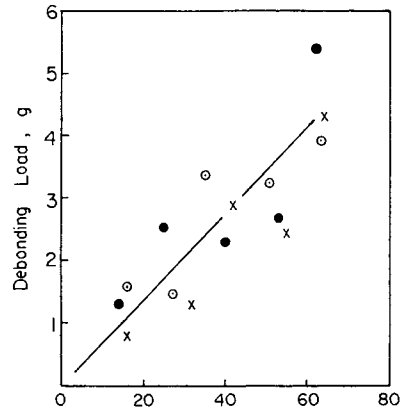
3A Length of Fiber Embedded in PEEK, μm



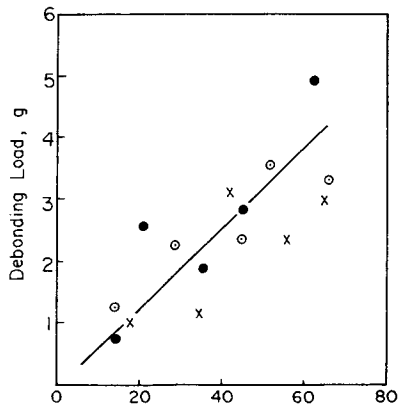
3B Length of Fiber Embedded in PEI, μm



3C Length of Fiber Embedded in PSF, μm



3D Length of Fiber Embedded in PES, μm



3E Length of Fiber Embedded in PPS, μm

Fig. 3. Debonding load vs embedded fiber length: (x) untreated carbon fiber, (O) PAA-1(2) coated carbon fiber, (●) PAA-2(2) coated carbon fiber.

The poor performance of PES may be a consequence of inadequate annealing of the testing specimen as mentioned before. The results from PPS seemed to suggest that brittle fracture occurred in the testing, although the fracture mechanism was not investigated in our experiment.

CONCLUSION

Polyamic acids improved the interfacial bonding between carbon fiber and aromatic thermoplastics. Their performance was found to be very selective. It depended not only on the chemical affinity between the bonding agent and thermoplastic resin, but also on the physical properties of both. Imidization of polyamic acids before bonding tended to reduce their bonding capability, unless the polyimides were sufficiently flexible.

Rigid thermoplastics of brittle nature were inherently weak at the interface. Even though interfacial bonding can be improved with a suitable bonding agent, reliable performance of the composites can hardly be expected since large variations in testing results were observed.

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