



MECHANISM ON FIXATION OF SURFACE AGENTS TO P-ARAMID FIBER FOR INTERFACIAL REINFORCEMENT IN COMPOSITES

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Abstract

An unique treatment for p-Aramid (PPT) fiber giving the interfacial reinforcement is predicted to prompt the permeation of agents into fiber and to make slits in PPT narrow together with hardening of agents by cross-link. In this study, the mechanism has been certified using X-ray diffraction, IR-ATR, and cup-and-pin method. X-ray diffraction of PPT fiber treated with agents indicates that the slits between crystallites is narrow by heating. It should be noted that treatment enhances the size of crystallite as large as in normal PPT fiber. This effect leads to the maintenance of fiber strength. IR-ATR analysis shows the permeation of the agent into the inner site of fiber. Cup-and-pin technique exhibits the hardening of film former only by mixing with silane in high temperature above 100 °C. These results support the mechanism describe above.

1 Introduction

Poly (*p*-phenylene telephthalamide) (PPT) is well known as a reinforcing fiber for composite materials. However, the interfacial strength is too weak to raise total performance of the composite, though some surface modification methods have been proposed, including plasma treatment [1, 2] and chemical modification [3, 4]. These modification methods cause the fibrillation of fiber and results in the reduction of fiber strength.

In the previous papers [5-7], a novel treatment for PPT fiber has been applied to reinforce the interface between fiber and resin in composites. This treatment also keeps the fiber strength. In the treatment, the sizing agents consists of silane coupling agents and film formers, which are normally used as sizes for the surface treatment of glass fiber. PPT fiber is modified during fiber

spinning to have a lot of large slits between crystallites along a filament. We call it open-structured PPT fiber. This state is considered to take a stable intermediate before making the final crystallite of PPT with narrow slits along fiber such as Kevlar 29[®]. In the treatment of open-structured PPT fiber, there are two steps to accomplish the fixation of sizes to the fiber, that is, permeation of sizes into PPT and heating of PPT. Considering the improvement of mechanical properties by the treatment, the following change is supposed in a filament: The first step prompts the permeation of the agents into open slits between crystallites in PPT by supercritical fluid method or by dipping method. The second step makes slits between crystallites narrow and forms networks structure with silane molecules and film former.

In this study, these steps have been confirmed using X-ray diffraction, IR-ATR, and cup-and-pin method. The first measurement evaluates the change of crystallite size that means the change of slit size. The second analysis determines the permeation depth of sizes into PPT fiber from the surface to evaluate the degree of permeation of sizes between normal and open-structured PPT fiber. The last method detects the change of viscoelasticity of the mixture of silanes and film former.

2 Experimental

2.1 Surface Treatment

PPT fiber used was specialized with a larger slit between crystallites in fiber structure (open-structured PPT) by the improvement of spinning system of PPT. KEVLAR[®] 29 and KEVLAR[®] 49 were used as references in this paper. Sizing agents were used as emulsion solution including silanes and film formers. In a typical case, film former was epoxy binder (EB) that was supplied as a

Table 1 Improvement Percentage of Interfacial Shear Strength by Different Impregnation Methods with Sizes to Open-structured Fiber *

Sizes	APS	UB	APS+UB
Dipping	-17	-1	13
Supercritical Fluid	19	23	67

* Fiber was heated at 170 °C after size impregnation. Interfacial shear strength of Kevlar[®] 29 was used as a reference value. Matrix was epoxy

commercial grade 6C1008, Nippon NSC Co. Ltd. Silane was γ -aminopropyltriethoxysilane (APS) that was purchased as a commercial grade KBE 903 from Shin-Etsu Chemical Co., Ltd. APS and EB was mixed and diluted in water to make 0.5 w/w% of APS and 2.5 w/w% of EB in aqueous emulsion. Instead of EB, urethane binder (UB), Vondic 1310F, Dainippon Ink and Chemicals Inc., was used.

In supercritical carbon dioxide fluid, the emulsion was solidified by freeze-drying to be applied in the following procedure. To make molecules of agents permeated into the open-structured fiber, supercritical carbon dioxide fluid was employed at 250 bars and 150°C. In dipping method, open-structured fiber was dipped into the emulsion solution. Uptake of sizing agents was 46.8 mg/g-fiber in solid. After the permeation, the fiber was heated at 100°C for 20 min and further at 170°C for 30 min to close the gap, that is, to change into normal type of PPT fiber.

In addition, the super critical carbon dioxide fluid method was impossible to control the amount of sizes on the fiber. Even after the treatment, the amount was not determined by gravimetric analysis for small amount of size charge. On the other hand, the dipping method controlled the amount of sizes by squeezing the emulsion solution from the fiber after dipping. Gravimetric analysis evaluated the amount of sizes by weighing the solution on the fiber.

2. 2. Evaluation of Treated PPT Fiber.

Permeation of agents into the fiber was evaluated using FTIR-ATR method. A yarn of fiber was wound on an internal reflectance element (IRE) of Germanium. A couple of peaks due to EB at 1300 cm⁻¹ and 830 cm⁻¹ were used as indices for permeation of agents. Penetration depth (d_p) of infrared light from IRE to PPT calculated was 0.54 μ m at 1300 cm⁻¹ and 0.87 μ m at 830 cm⁻¹.

Cup-and-pin method was carried out using a thermal mechanical analyzer, DSC-22, Seiko Instruments Inc., to evaluate the formation of networks with silane and film former. Apparent viscoelasticity was determined from S-S curves of a pin in a cup filled with emulsion solution including silane and film former. Force was vibrationally applied to the pin at 5 mN of amplitude and 0.1 Hz of frequencies. In addition, FT-IR analysis was employed to detect the interaction between silane and film former at different temperatures.

The size of crystallite in the fiber was evaluated by a X-ray diffractometer equipped with a X-ray source and a CCD camera, Mercury CCD X-ray System, Rigaku Corp. The resulting peak shape due to crystal lattice (1 1 0) was used to determine the size of crystallites.

2.3 Evaluation of Mechanical Properties

To evaluate the mechanical properties such as adhesion of fiber to matrix resin and strength and modulus of composites, microdroplet test and bending test were performed. Matrix was epoxy resin, Epikote 828, used in both tests.

Table 2. Bending Properties of Unidirectional Fiber Composite with Sized PPT*¹

Sizes	Bending Strength/MPa	Bending Modulus / GPa
Normal PPT * ²	531	11.3
APS+UB* ³	581	11.2
APS+EB* ³	676	14.0

*¹ Treatment: dipping method

*² Untreated / Kevlar[®] 29

*³ Open-structured fiber treated by dipping method for size penetration

Table 3 Relative Intensity^{*1} of peak due to EB in sizing agents on treated PPT fiber detected by FTIR-ATR method.

PPT	at 1300cm ⁻¹	at 830cm ⁻¹	ratio of peak
	$d_p=0.54 \mu\text{m}$	$d_p=0.87 \mu\text{m}$	(at 1300 cm ⁻¹ / at 830 cm ⁻¹)
KEVLAR [®] 29	0.137	0.152	0.90
Open-structured	0.078	0.121	0.64

*1 calculated using peak intensity due to amide group of PPT as a reference

A microdroplet test machine, HM410, Tohei Industry Co., Ltd., was employed for measurement of interfacial shear strength. A filament was then taken out of a yarn of sized fiber. The resin was charged along the filament and then cured to make a lot of microdroplet on the fiber.

The bending test was performed to unidirectional fiber-reinforced composites, which has a shape of rod with 3 mm of diameter and 64 % of volume fraction.

3 Results and Discussion

3.1. Treatment Methods

Dipping and supercritical fluid methods are compared using APS only, UB only and the mixture of APS and UB (1:5 w/w). As shown in Table 1, the supercritical fluid method gives higher values in the interfacial shear strength, compared with the dipping method. In particular, the mixture of APS and UB gives the highest value. This means that the fixation of

sizes depends not only on the closing of gap and but also on the networks between APS and UB, as described in glass fiber – resin composites [8]. Thus, silane and film former molecules were linked each other in the narrow gap resulting from the heating process, and such linked agents were impossible to release from the gap even when it is interacted with matrix resin at the surface of PPT fiber.

This effect of adhesion of sized PPT fiber on matrix resin improves the mechanical properties of composites, as shown in Table 2. The mixture of APS and EB gives the highest value in bending strength and bending modulus. The mixture of APS and UB indicates a lowering of the bending properties, compared with the mixture of APS and EB. This depends on the property of UB that is weak but elastic. However, those mixtures gives higher values in bending properties, compared with Kevlar[®] 29 as a reference of normal PPT fiber unsized. This means that the treatment with silanes and film formers gives interfacial reinforcement to composites.

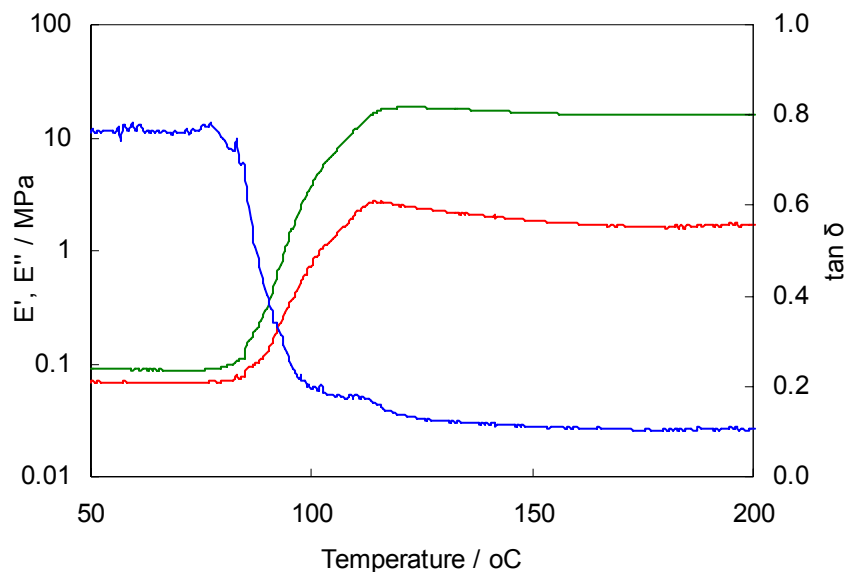


Fig. 1. Temperature dependence on apparent viscoelasticity of a pin contacted with sizing emulsion in a cup; E' (-), E'' (-), and tan δ (-).

3.2 Permeation of Sizes into PPT Fiber

IR-ATR analysis has detected peaks at 1300 cm^{-1} and 830 cm^{-1} due to EB in sizing agents treated on PPT fibers; open-structured PPT and KEVLAR[®] 29. The peak intensities in each fiber is listed in Table 3. Open-structured PPT gives low intensities, compared with KEVLAR[®] as a normal type of PPT fiber. Considering the penetration depth that is shorter than the diameter of fiber, $12\text{ }\mu\text{m}$, open-structured PPT easily makes the agents permeated into inner part in the fiber. This is also supported from the comparison between peak intensities at different frequencies. The ratio of peak intensity at 1300 cm^{-1} to that at 830 cm^{-1} is near one in KEVLAR[®] 29, while is lower in open-structure PPT. This means that agents are deeply permeated into the fiber. This suggests that there are open slit or open space where small molecules are easily penetrated.

3.3 Network between Silanes and Film Formers

Cup-and-pin technique is generally employed to evaluate the hardening temperature for thermosetting resin. In this case, this technique is also used to know if the mixture of silanes and film formers is hardened in temperature range during heating process in the treatment of PPT fiber. Silanes and film formers themselves show no hardening between room temperature and $200\text{ }^{\circ}\text{C}$ by cup-and-pin method. On the other hand, the mixture

of silanes and film formers makes a hardened solid. The apparent viscoelasticity has been calculated by utilizing adhesion between the pin and the mixture.

As shown in Fig. 1, the apparent viscoelasticity shows rubber-like property above $100\text{ }^{\circ}\text{C}$. This suggests that film former is linked with silanes. In addition, FT-IR has been employed to obtain the change of functional group of silanes and film formers. In the mixture of APS and EB, peak intensity due to epoxy ring and primary amino group of APS decrease with temperature, while peak intensity due to secondary amino group and siloxane bond increase with temperature, as shown in Fig. 2. As a result, APS is found to be reacted with EB. This means that APS and EB in the mixture make network structure after permeation into slit in PPT fiber.

3.4 Crystallite Size by X-ray Diffraction

X-ray diffraction has been applied to know the size of crystallites and the crystallinity of fiber for open-structured PPT treated with the mixed agents. The crystallinity gives approximately 90 % in all kinds of PPT fiber; normal PPT fiber (KEVLAR[®] 29 and KEVLAR[®] 49) and open-structured fiber regardless of treatment. As very well known, normal PPT fiber has high crystalline polymer. Open-structure PPT is also found to keep the high crystallinity.

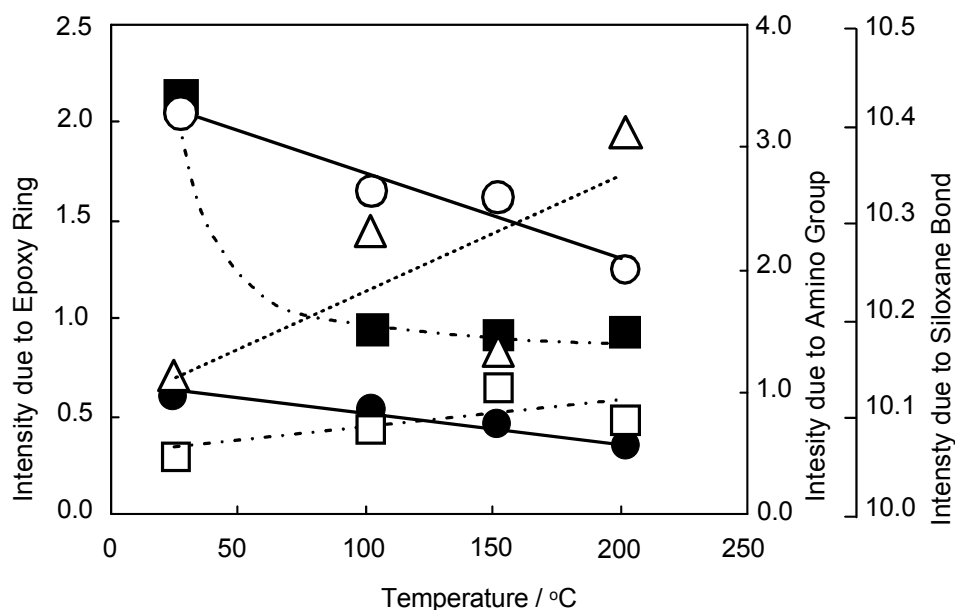


Fig. 2. Change of absorbance at 910 cm^{-1} (○) and 860 cm^{-1} (●) due to epoxy ring of EB, at 1580 cm^{-1} (■) due to primary amino group of APS, 1520 cm^{-1} (□) due to secondary amino group of APS, and at 1100 cm^{-1} (△) due to siloxane bond.

Table 4. Change of Crystallites Size with different types of PPT Fiber measured by X-ray Diffraction

Sample	Crystallite	
	Sheet / hkl	Size / nm
Normal PPTA	110	6.0
	200	5.0
	004	6.6
Open Gapped PPTA	110	3.6
	200	4.6
	004	6.7
Open Gapped PPTA after Heating	110	6.8
	200	5.2
	004	6.9

The size of crystallite is calculated from the shape of crystal lattice (110), as listed in Table 4. The crystallite size are different in every type of PPT fiber. The size increases in the order of open-structured fiber, KEVLAR[®] 29, open-structured fiber after heating, open-structured fiber after treatment, and KEVLAR[®] 49. Considering the crystallinity of PPT fibers, this change means that the width of slits between crystallites decreases in this order.

Open-structured PPT with a large slit changes to the structure like normal PPT fiber, that is, KEVLAR[®] 29 in heating process in this study, as described previously. However, it should be noted that the treatment elevates the size of crystallite as large as in enhanced PPT fiber, that is, KEVLAR[®] 49. This means that agents permeated into fiber have a role in enhancement of fiber. This effect leads to the maintenance of fiber strength regardless of the treatment, as described previously [5].

4 Conclusion

A novel treatment of PPT fiber that gives excellent effect on interfacial reinforcement of composites has been examined using FT-IR, cup-and-pin technique, and X-ray diffraction to clarify the mechanism on fixation of sizing agents to PPT fiber. Consequently, sizing agents consisting of silanes and film formers are easily permeated into open-structured PPT fiber with large slits between crystallites. In heating process, open-structured PPT fiber makes the slit closed together with sizing agents. The agents is linked to make a large size of molecules. As a result, sizing agents are difficult to release from the fiber. In addition, such a large of

linked sizing agents promotes the growth of crystallites in the fiber, and maintains the fiber strength.

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