METHOD OF PRODUCING COMPLEX SHAPED COMPOSITES WITH XYLYLENEDIAMINE DERIVED POLYAMIDE MATRIX

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Abstract

A specialty polyamide, poly-xylylenesebacamide (XD10) known as LEXTER®, has excellent mechanical properties, low water absorption, chemical resistance, suitable crystallization speed, and is bio-based. These properties are maintained when they are used as matrix resins of carbon or glass fiber reinforced thermoplastics (C/GFRTP). In this study, XD10 was applied to a novel composite. These polyamide and carbon or glass fiber composites promised to achieve light-weight, low-cost and recyclable composite parts, since tooling needs were minimal and material waste was virtually non-existent. This manufacturing process is composed of commingling, tailored-fiber placement (TFP), and light-molding methods. First, finely dispersed and pre-impregnated commingled yarns made of carbon fiber and XD10 fiber were prepared in several conditions. Secondly, the commingled yarns were placed using the TFP method. The relationships between the manufacturing conditions of commingled yarns and TFP handling properties were tested. The ideal flexibility and sturdiness of commingled yarn using the TFP method was determined. Finally, the preform was made. The optimized commingled yarn was arranged with circular and radial patterns by the TFP method. It was then set into a silicone mold and exposed to infrared light under a vacuum condition for consolidation. An obtained CFRTP molding was well-impregnated, even under the vacuum condition, because of the use of pre-impregnated commingled yarn. It was confirmed that CFRTP moldings with complicated geometry could be obtained using these materials and methods.

Background and Requirements

Fiber reinforced plastics (FRP) have been used in various industries for long time. Among them, glass fiber reinforced plastics (GFRP) are very common materials for enhancing their mechanical properties and compatibility with resins.

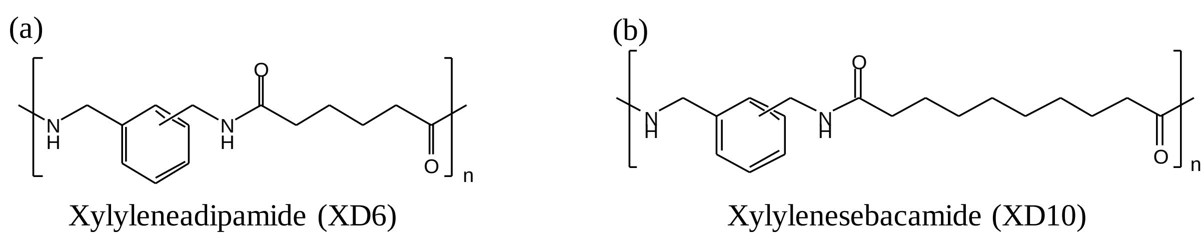

Figure I: Chemical Structures of Polyamides Derived from Xylylenediamine.

The chemical structures of xylyleneadipamide (XD6) and xylylenesebacamide (XD10) are shown in figure 1. XD6 (Fig. 1(a)) is composed of xylylendiamine and adipic acid, and XD10 (Fig. 1(b)) is composed of xylylendiamine and sebacic acid. Because of the combinations of aromatic groups and aliphatic groups, they obtained unique properties such as high strength and elasticity, low water absorbability, gas barrier properties, heat resistance, and recyclability.(1-3) The basic properties of XD6 and XD10 are shown in table 1 below. The melting point of XD6 is 237 ºC. On the other hand, XD10, LEXTER®, has three grades with different thermal properties; LEXTER 8000, 8500, and 8900. Though the basic ingredients are the same, the crystalline structures are controlled to express different melting points from 190 ºC to 290 ºC. XD10 is a bio-based polyamide. As sebacic acid is produced from castor beans, the effects from CO2 emissions on the environment are much less compared to conventional fossil-based polyamides. While being environmentally friendly, XD10 has achieved many characteristics unmatched by existing bio-based resins; for example, its moisture absorption rate is considerably lower and keeps its mechanical properties even after water absorption. Figure 2 shows plots of several polyamide resins on melting points and bending moduli. It is remarkable that XD6 is one of the hardest resins among super-engineered plastics. Among resins with the melting point below 200 ºC, LEXTER 8000 has the highest modules. LEXTER 8500 has a good balance of processing conditions and heat resistance and has many wide applications. LEXTER 8900 has a high melting temperature and a high crystallization speed. Its mechanical properties remain unchanged in water environments.

Table I: Basic Properties of Polyamides Derived from Xylylenediamine.

Resin	Grade	Melting Point, ºC	Glass Transition Point, ºC	Bending Modulus, GPa	Bending Strength, MPa	Density, g/cm^3	Saturated Water Gain, %
XD6	#6000	237	85	4.4	160	1.22	5.8
XD10	LEXTER 8000	190	60	3.2	136	1.13	2.5
	LEXTER 8500	213	63	2.9	135	1.13	2.5
	LEXTER 8900	290	75	2.9	122	1.13	2.6

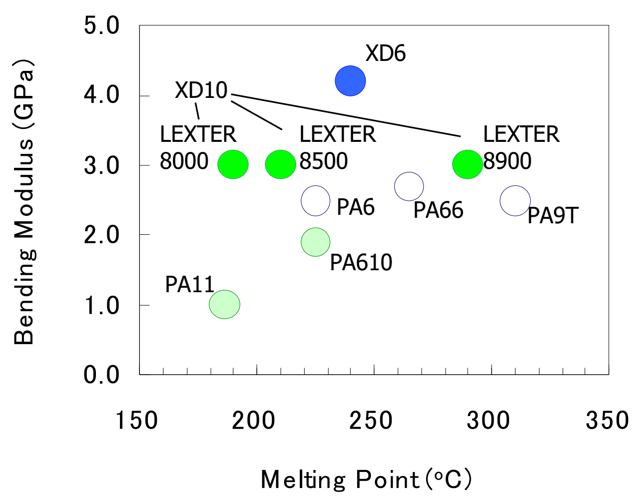

Figure 2: Plots of polyamides on a scale of melting points and moduli.

XD6 and XD10 can also be used as a matrix resin of carbon fiber reinforced plastics (CFRP). Low water absorption, high moduli, and high strength are properties produced in the CFRP application. Water absorption curves are shown in figure 3. The water absorbing ratio of XD6 was slow. That of XD10 was even slower and the water content of XD10 after 600 days remained under 3%. These characteristics negate the trouble of having to use water condition controls and allow for better production of prepregs. Moreover, they generate less water vapor during molding processes. Mechanical properties of CFRP using XD6 and XD10 as matrix resins are shown in Table 2. XD6-CFRP has one of highest mechanical properties including thermosetting CFRP.

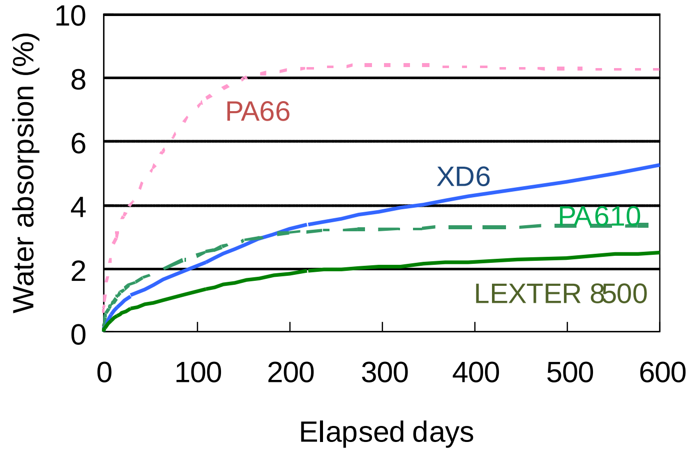

Figure 3: Water Absorption Curves of Polyamide Resins dipped in water at 23 °C.

Table II. Mechanical Properties of XD6- and XD10-CFRP, Uni-Direction.

Resin	Tensile		Bending		Volume of fiber (V_f)
	Modulus, GPa	Strength, MPa	Modulus, GPa	Strength, MPa	%
XD6	121	2660	112	2613	57
XD10	117	2059	110	2208	56

In conventional methods of making CFRP product, UD tapes and stamping boards are widely used. UD tape is laid onto a substrate and laminated by ultrasonic wave or lasers. When manufacturing a complex-shaped product, corners have to be cut off, as UD tape is rectangular. Thus, it is preferred to use the exact amount of materials on the exact product shape. In addition, low-cost molding processes are needed in the productions of many small quantity models, industrial prototyping, and academic exercises, in particular. In this study, XD10 was applied to a novel composite, which promised to achieve minimal tooling needs and emission.

EXPERIMENTATION

Materials

Polyamide fiber: XD10 LEXTER 8500 (Mitsubishi Gas Chemical Co. Inc.). Carbon fiber: TR50S (Mitsubishi Chemical Corp.). Commingled yarn: Dualon (Kajirene Inc.). Substrate for fiber placement: LEXTER 8500 film 50 μm thickness. Stitching fiber: Aramid fiber (Kevlar#30 200D 1x2 Z (Du Pont-Toray Co., Ltd.)), Polyamide fiber (LEXTER 8500).

Processing Machines

Preform fabrication: Tailored-Fiber Placement (Tajima Inc.). Molding machine: Light-Molding System, Amolsys (D-MEC Ltd.)

RESULTS

Molding Process Overview

Polyamide XD10 fiber was prepared to be suitable for commingling with carbon fiber[4] The resin fiber was highly dispersed into a carbon fiber yarn. The surface of the commingled yarn was treated specially for the convenience of the following processes without losing their textile working abilities. The commingled yarn was appropriately placed on a polyamide film by tailored-fiber placement[5]. The direction of carbon fiber was precisely controlled. The well-placed preform was cured by Amolsys System. The preform was put into a silicone mold and heated by near-infrared light for consolidation under vacuum conditions. After cooling, the objective was obtained. This molding process was a challenge when using thermoplastic, because there had not been a commingled yarn which could be used in tailored-fiber placement, and it was too difficult to impregnate thermoplastic resin using light-molding, as it could apply atmospheric pressure, though thermoplastic resin usually needed more than 10 times the amount of high pressure.

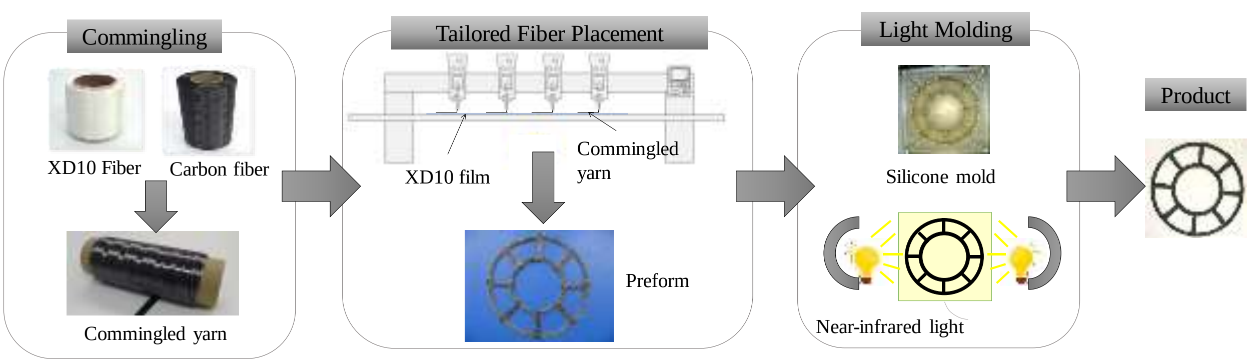

Figure 4: General description of the molding process.

Commingled Yarn

In the commingled yarn containing the continuous reinforced fibers and the continuous resin fibers, such continuous reinforced fibers and such continuous resin fibers are required to be thoroughly dispersed for faster impregnation. In view of improving the dispersion, it is preferable to control the amount of consumption of treatment agents, such as surface treatment agents and bundling agents (also referred to as oil agents or sizing agents). If, however, the amount of treatment agents is too small, the continuous reinforced fibers and the continuous resin fibers would become less adhesive and would result in fiber separation. Moreover, the commingled yarn is required to be moderately flexible, since the commingled yarn is not a final product.

Flexibility of a commingled yarn was controlled by heat treatment conditions on the yarn. Adding heat, the commingled yarn starts impregnating and gets more bundling properties but loses flexibility. The optimized heating conditions were tested. Flexibility was evaluated by the tensile load of pulling commingled yarn through a polyamide tube with a small hole for squeezing yarn. Figure 5(a) shows a measuring apparatus, and figure 5(b) shows the relationships between tensile loads and amounts of heat. Tensile loads increased when commingled yarn was heated more than a certain amount, which indicated commingled yarn lost its flexibility with excessive heat.

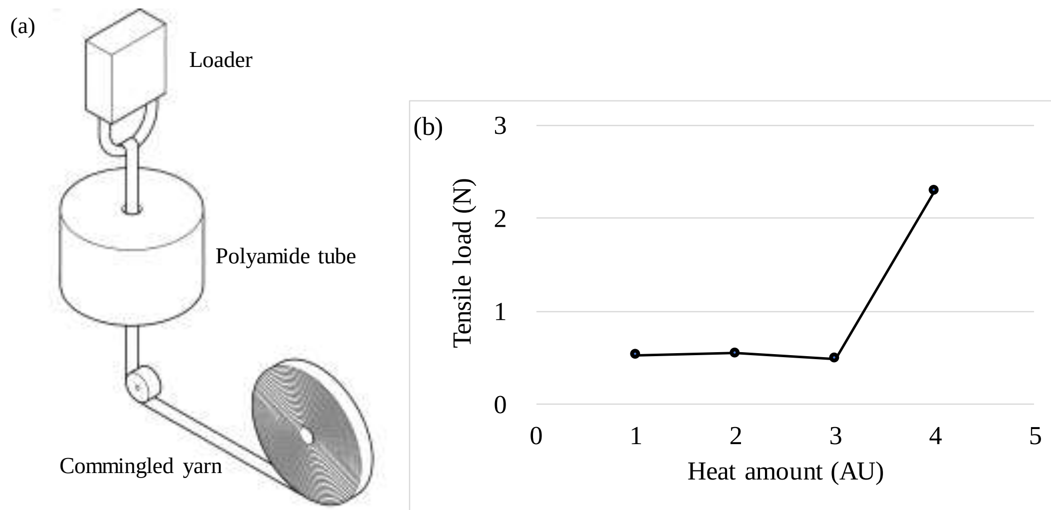

Figure 5: Flexibility measurement apparatus (a). Relationships between tensile loads and heat amounts (b).

Bundling properties were evaluated by heat-shrinkage tests. Commingled yarn treated with heat was set on a frame shown in figure 6 and heated at 220 ^{o}C for 10 minutes. The difference in length of commingled yarn was measured and the shrink ratio was calculated from equation 1. The relationships between shrink ratios and heat amounts are shown in figure 7. Initial length of commingled yarn (L) was 300 mm. A commingled yarn with a low shrink ratio has good bundling properties. Commingled yarns treated with heat amounts of 3 and 4 gave low shrink ratios.

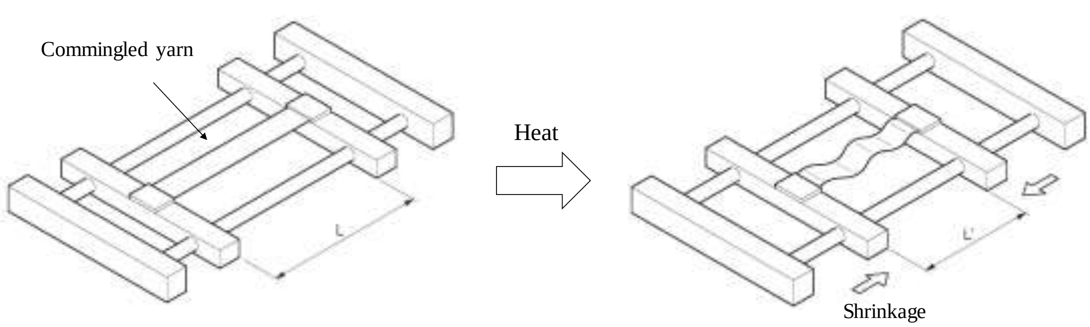

Figure 6: Measurement of shrink ratios of commingled yarn.

$$\text{Shrink ratio (\%)} = ((L-L')/L) \times 100 \qquad (1)$$

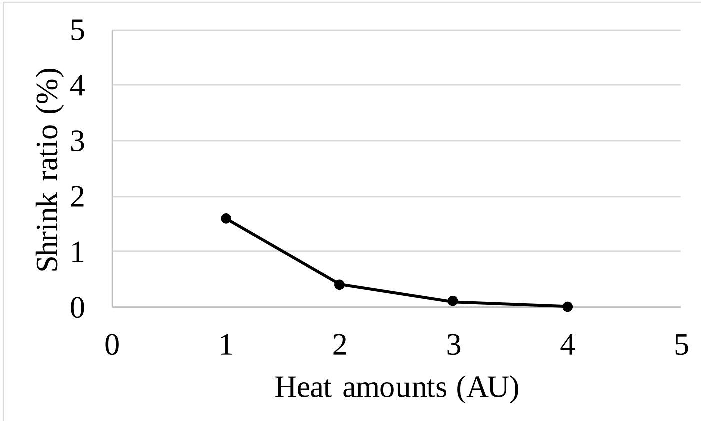

Figure 7: Relationships between shrink ratios and heat amounts.

Commingled yarns were laid in uni-direction and pressed at 220 ^{o}C under 3 MPa for 3 minutes. Their impregnation properties were observed. Cross-sectional photographs of UD-materials are shown in figure 8. UD-materials using commingled yarn treated with heat amounts of 3 and 4 were fully impregnated, indicating heat treatment on commingled yarn improved impregnation properties.

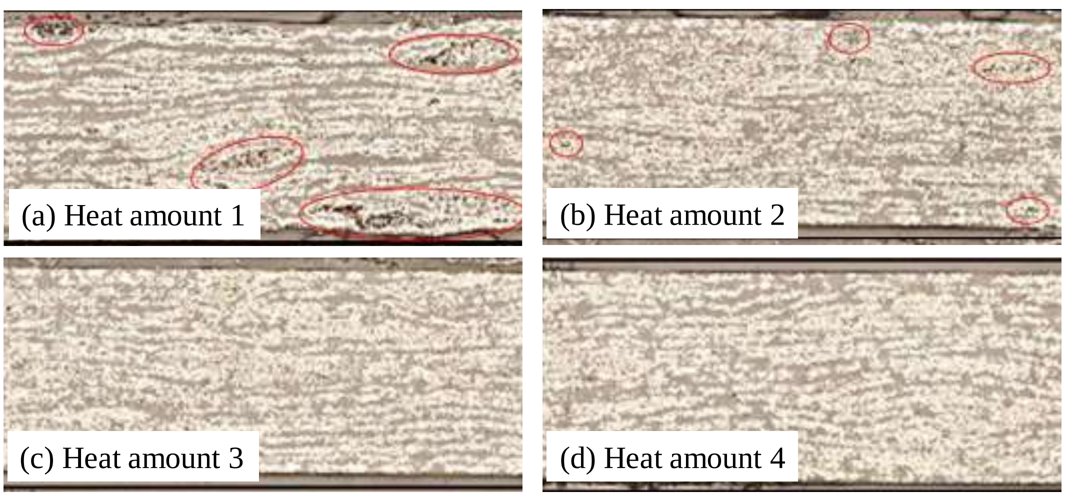

Figure 8: Cross-sectional photographs of UD-materials. Circles show un-impregnated areas.

Considering flexibility, bundling and impregnation properties, commingled yarn treated with heat amounts 3 met all necessary needs to begin processing. A cross-section SEM of a commingled yarn heat amount 3 showed that there were impregnated regions on the surface and free-fiber regions between them. It is considered that impregnated regions kept a yarn bundled, and free-fiber regions make the yarn flexible. This commingled yarn would be preferable for textile processes such as weaving, braiding, and tailored-fiber placement.

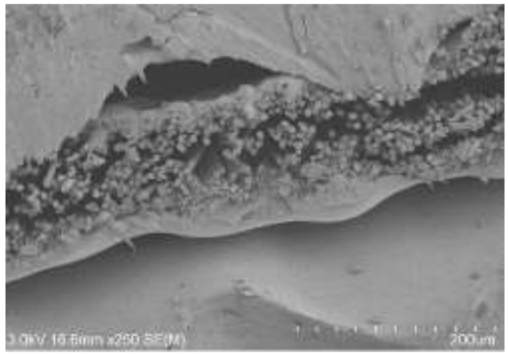

Figure 9: Cross-sectional SEM observation of commingled yarn with both flexibility and bundling properties.

Tailored-Fiber Placement

Commingled yarns were applied to tailored-fiber placement (TFP). Polyamide film was used as a substrate. Aramid fibers and polyamide fibers were used as stitching fibers. Complex-shaped molding samples can be made by this processing system. Commingled yarn was stitched on a polyamide film. The direction of carbon fibers was accurately controlled by this system. Furthermore, as the stitching process generated less waste, cutting processes and material costs could be saved.

Figure 10: Tailored-fiber placement of commingled yarn.

A propeller-like article was made. It was difficult to use a low-bundled yarn (heat amount 1) because the yarn easily separated during the TFP. It was also difficult to use yarn with low flexibility (heat amount 4), because the yarn was too hard and fragile to follow a line that the TFP machine made, on edges in particular. Using a flexible and well-bundled yarn, it was perfectly placed onto a polyamide film without breakage and separation of commingled yarn.

Table III: Usability of commingled yarn prepared by treating different heat amount.

Commingled yarn Heat amounts	1	2	3	4
Flexibility	Good	Good	Good	Poor
Bundling properties	Poor	Ok	Good	Good
TFP usability	Poor	Ok	Good	Poor

Comparing to a widely used UD tape placement method[6], commingled yarn is flexible enough and is able to draw circles without breaking continuous carbon fibers. On the other hand, UD tape placement method cannot withstand a difference between internal diameter and outer diameter. In addition, it is considered that carbon fibers of UD tape are cut during milling out a shape. In case of manufacturing a complex shape with narrow parts, a product yield is raised, as shown in figure 11. The width of UD tape is assumed to be 20 mm.

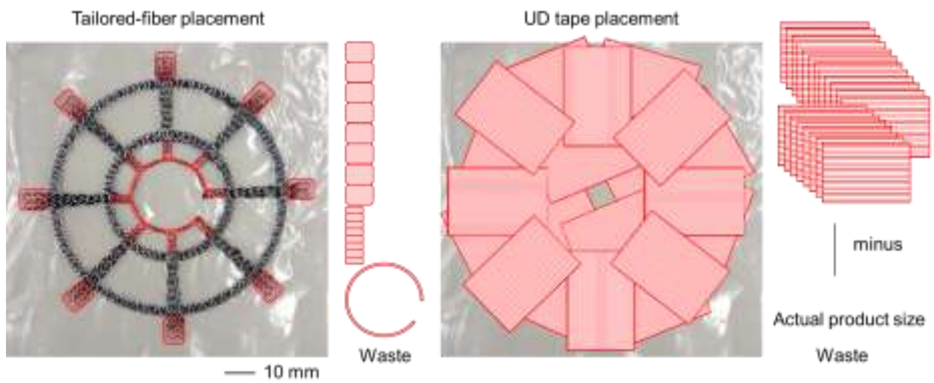

Figure 11: Difference of product yield of TFP and UD tape placement.

Light-Molding

The well-placed preform was cured by the light-molding system, Amolsys. The preform was put into a silicone mold and then heated using near-infrared light under vacuum conditions for impregnation. After cooling, the objective was obtained. As resin fibers and carbon fibers were mixed thoroughly in commingled yarn, it was enough to form a finely-molded product under vacuum conditions.

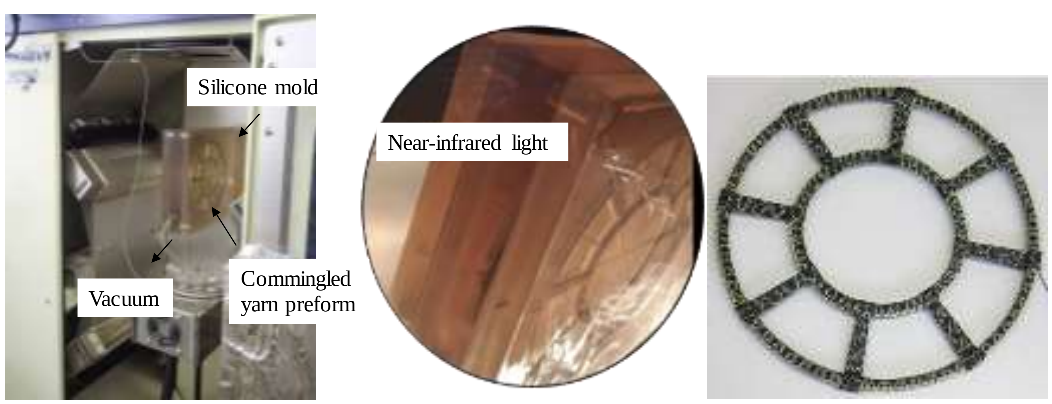

Figure 12: Light-molding system and consolidated yarn.

Properties of Molded Articles

In order to investigate the effect of stitching fibers on impregnation properties during molding, the impregnation state was quantified by cross-sectional observation of various specimens. In addition, a tensile test using UD specimen was carried out to investigate the effect of stitching fibers on mechanical properties. Uni-directional preform, having a length of 200 mm and a width of 20 mm, was produced and pressed to prepare a specimen. The effect of existence of stitching fibers on impregnation properties after molding was examined by using polyamide fibers that had been melted during the molding process and aramid fibers that had not been not melted as stitching fibers. UD specimens were molded by the following conditions; at 260 °C, under 3 MPa for 3 min. Furthermore, the effect of using the TFP technology on mechanical properties was examined by comparing the un-impregnation ratio and the mechanical properties with non-stitched specimens.

Un-impregnation ratio from the cross-sectional observation of each specimen is shown in figure 13. The un-impregnation ratio in all specimens was less than 0.6%, but in the specimen with aramid stitching fibers, the un-impregnation ratio was slightly higher than the other specimens. From this result, unlike polyamide, the aramid stitching fibers does not melt by the heat during molding and remains in the specimen. Therefore, the impregnation state of the specimen would be affected by the remaining stitching fibers in the specimen. As a result, it seemed that the waviness of commingled yarn was generated, commingled yarn was tied up and V_f in commingled yarn was increased by the stitching fibers, as compared with the non-stitched one. Therefore, more molding time or molding pressure or molding temperature will be needed for better impregnation states for the molding with TFP preform due to the increase of V_f in the fiber bundle by stitching fibers.

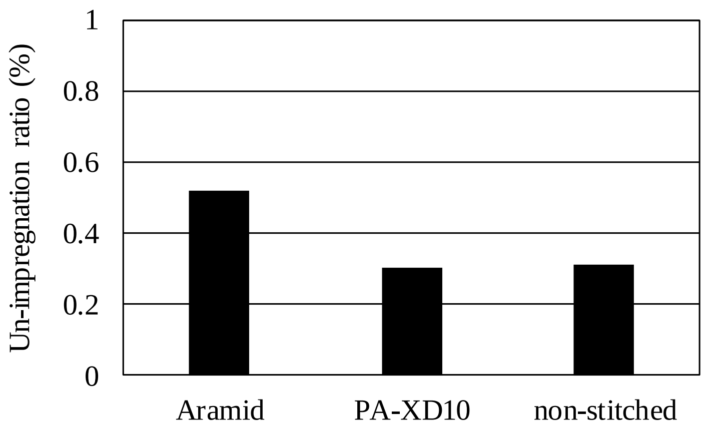

Figure 13: Un-impregnation ratio of various specimens.

In order to investigate the effect of stitching fibers on mechanical properties, a tensile test was conducted for various specimens. The achievement ratio of mechanical properties to the theoretical value of each specimen is shown in figure 14. The achievement ratio is the ratio of measured value to the theoretical elastic modulus and strength in the 0-degree direction obtained from the rule of mixture with V_f set at 50%. As shown in figure 14, the achievement ratio of elastic modulus is more than 90% in all specimens. The achievement ratio of tensile strength for all specimens was also about 70% and a few percent difference was shown by the specimen. In previous studies, the un-impregnation ratio of less than 1% did not affect the strength of the composite material. Consequently, the difference in structure of reinforcing fibers due to the stitching fibers does not affect the strength.

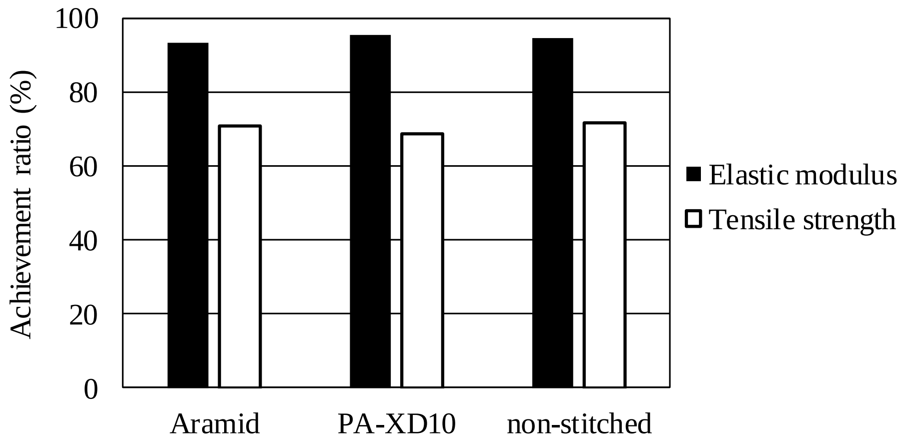

Figure 14: Achievement ratio of mechanical properties to the theoretical value.

Summary and Next Steps

Low water-absorption, high mechanical properties polyamide XD10 was used for CFRTP. Well-dispersed commingled yarn consisting with both conflicting properties, flexibility and bundling properties, were developed by providing proper heat amounts. Commingled yarn could be used in tailored-fiber placement and light-molding systems, which had not been achieved for thermoplastic materials in the past.

This process is especially effective for the production of many products in small quantities, because the design of products can easily be changed by fiber placement methods, and the silicone mold for light-moldings are much less expensive than metal molds for the conventional heat-press processes. Next, the increase of production efficiency is being investigated, as an example, controlling the fineness of commingled yarn, adding needles at tailored-fiber placement, optimizing the combination of a prepreg type and a curing system.

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