

XYLYLENDIAMINE DERIVED POLYAMIDE RESIN FOR HIGH MECHANICAL STRENGTH COMPOSITE MATERIAL

Nobuhiko MATSUMOTO, Nobuya SAEGUSA, Jun MITADERA

Mitsubishi Gas Chemical co., Inc.

Abstract

Condensation polymers of xylylenediamine with adipic acid (XD6) or sebacic acid (XD10) are highly functional polyamides that offer high mechanical strength, high modulus, high chemical resistance, and low moisture absorption. As XD6 and XD10 had good interfacial adhesion with carbon fiber and glass fiber, composite materials using these polyamides showed excellent mechanical properties without sacrificing other qualities. In particular, XD6 reinforced carbon fiber brought out the high mechanical properties, which were almost reaching the theoretical values. On the other hand, XD10 was characterized by its extremely low water absorption properties compared with other polyamides, thus, would be suitable to be used in high humid environments. These polyamides were converted into several prepregs, and various types of molding were tested. They showed excellent moldability in any conventional and the latest molding methods. It is considered their thermal properties, crystallization behavior, and moisture absorption are within a proper range.

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.

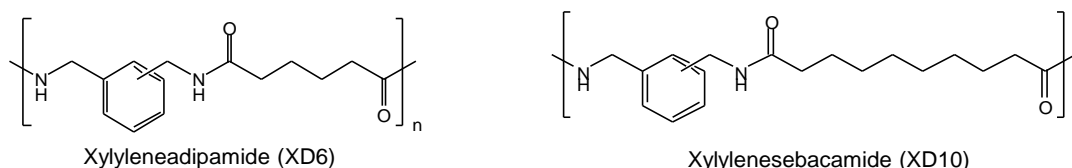


Figure 1: Chemical Structures of Polyamides Derived from Xylylenediamine.

The chemical structures of xylyleneadipamide (XD6) and xylylene-sebacamide (XD10) are shown in figure 1. XD6 is composed of xylylendiamine and adipic acid, and XD10 is composed of xylylendiamine and sebacic acid. Because of the combinations of aromatic group and aliphatic group, they obtained unique properties such as high strength and elasticity, low water absorbability, gas barrier property, heat resistance, and recyclability.⁽¹⁻³⁾ The basic properties of XD6 and XD10 were shown in table 1. The melting point of XD6 is 237 °C. On the other hand, XD10, LEXTER®, has three grades with different thermal properties, LEXTER 8000, 8500, and 8900. Though the basic ingredients are same, the crystalline structures are controlled to express different melting points from 190 °C to 290 °C. XD10 is bio-based polyamide. As sebacic acid is produced from castor beans, CO₂ emission to the environment is 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 low and keeps its mechanical properties even after moisture absorption. Figure 2 shows plots of several polyamide resins on melting point and bending modulus. It is remarkable that XD6 is one of the hardest resins among super engineering plastics. LEXTER 8000 has the highest modulus resin bellow the melting point of 200 °C. LEXTER 8500 has a good balance of processing condition and heat resistance, and has wide applications. LEXTER 8900 has high melting temperature and high crystallization speed. Its mechanical properties stay in water environment.

Table 1: Basic Properties of Polyamides Derived from Xylylenediamine.

Resin	Grade	Melting point (°C)	Glass transition point (°C)	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	215	63	2.9	135	1.13	2.5
	LEXTER 8900	290	75	2.9	122	1.13	2.6

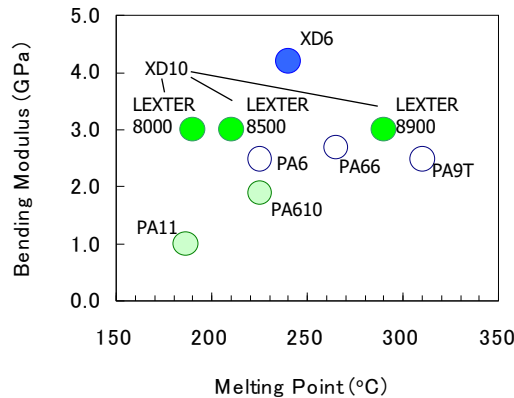


Figure 2: Plots of Polyamides on a Relation of Melting Point and Modulus.

Focusing on thermoplastics, XD6 based GFRP, as known as Reny®, has been used since 1980's.⁽⁴⁾ For a few decades, however, further mechanical properties have been required to FRP materials, and advanced materials such as continuous glass fiber reinforced thermoplastics (c-GFRTP) and continuous carbon fiber reinforced thermoplastics (c-CFRTP) have been developed. As a matrix resin, polyamide 6 (PA6), polypropylene (PP), and super engineering plastics have been commonly used. PA6 has good compatibility with reinforcing fiber, and good impregnation property in addition to high mechanical property, while its water gain brews up problems of mechanical properties and dimensional stability. PP is superior to anti-humidity, although its FRTP is not good enough at mechanical and thermal properties. Using super engineering plastics, e.g. polyetheretherketone and polyimide, as a matrix resin, high performance FRTP materials can be obtained, although their processing conditions are so severe that only the high performance processing machines can mold them. In order to solve these problems, FRTP using XD6 and XD10 as matrix resins was studied.

c-FRTP Prepregs using XD6 and XD10 as Matrix Resin

Generally, prepregs are used to produce c-FRTP moldings. The major prepregs would be uni-direction tape (UD tape), fiber lamination sheet, commingled yarn, and non-woven fabric. XD6 and XD10 were tried to produce these four prepregs.

UD Tape.

UD tape is a roll of resin film, on which glass or carbon fibers are on or in the resin film. First, XD6 and XD10 film were molded, and then widely opened carbon fibers were attached on the film. Differed from conventional polyamide film, XD6 and XD10 films did not absorb much water in air during a process, thus stable and prolonged operation was possible even under high humidity condition. The UD tapes were laminated in same direction, and pressed at 280 °C to obtain 0.5 mm thickness specimens. As shown in table 2, XD6-CFRP has excellent mechanical properties, which almost reach a theoretical strength calculated based on law of mixture⁽⁵⁾; tensile modulus 135 GPa, tensile strength 2831 MPa. It is considered that XD6 is so strong that it does not easily give the opportunity of a first break. Indeed, on bending test, the surface of compression side of XD6-CFRP did not break, in contrast to most CFRP materials that started breaking at a surface of compression side.



Figure 3: UD Tape of XD10-CFRP.

Table 2: Mechanical Properties of XD6- and XD10-CFRP, Uni-Direction.

Resin	Tensile		Bending		Vf %
	Modulus GPa	Strength MPa	Modulus GPa	Strength MPa	
XD6	121	2660	112	2613	57
XD10	117	2059	110	2208	56

Carbon/Glass Fiber Lamination Sheet.

A reinforcing fiber lamination sheet impregnated with XD6 or XD10 is rigid and strong. It can be formed adding by heat and press. It is mainly made by hot pressing a lamination of fiber cloths and resin films or powder. It is to be noted that the resin should not contain much water, because water may stay at an interface between fiber and resin, and weaken a lamination sheet. XD10 is so a hydrophobic resin that it inhibits such a problem, comparing to conventional polyamide.



Figure 4: Lamination Sheets and a Formed Lamination Sheet from SPIC co.

Commingled Yarn.

A commingled yarn is composed of carbon fibers and resin fibers dispersing in high level. In molding, resin fiber melts and forms matrix. A commingled yarn takes short impregnation time because impregnation starts everywhere inside the yarn. Furthermore, as it is a flexible yarn, textile processing is available. Thus, it is able to be used for various styles such as woven fabric, knitted composite, and tubular braided composite. These fabrics are highly drapable, and easy to obtain a complex shape product. Water content of XD6 fiber and XD10 fiber is 3.2% and 1.7%, respectively, and that of PA6 is 4.1%. Considering water control is important to create FRP products, XD10 is a suitable resin for commingled yarn.



Figure 5: Commingled Yarn and Its Textile from Kajirene Inc.

Non-Woven Fabric.

A non-woven fabric is the most cost saving prepreg. Although the mechanical properties are not as high as the three prepreps above, it is isotropic and it has great drapability. As mentioned in the former paragraph, low water absorbing property is an advantage for XD6 and XD10. A non-woven cloth can be used by itself, however, the combination with UD tape or fiber sheet dramatically improves mechanical property.



Figure 6: Non-Woven Cloth of Carbon Fiber and XD10 fiber (left). Enlarged View of the Cloth (right) from ITC co.

500 μ m

c-FRTP Moldings using XD6 and XD10 as Matrix Resin

c-FRTP using XD6 and XD10 are excellent in molding process. Almost all of the molding methods are acceptable.

Figure 7 shows a part of automobile made of UD Tape and aluminum. Thermo Assisted Molding (TAM, CAP co.) method was applied. Cycle time was circa 3 minutes. Both a strength and dimension were fine.



Figure 7: Automobile Parts Made of UD Tape (front), and Aluminum Die-casting (behind) from CAP co.

Figure 8 shows a compression molding of a motorbike part. Chopped UD tape was put randomly on a mold. The mold was pressed for 1 min at 250 °C. This method is simple, fast, isotropic, strong, and high fluidity so that ribs and bolt holes were well formed. Its modulus and strength were 20 GPa and 450 MPa, respectively, those are as good as aluminum die cast.



*Figure 8: Chopped UD Tape (left) and Its Compression Molding of a Part of Motorbike (right)
from Hamamatsu Society of CFRP Business R&D.*

Figure 9 shows an automobile part made by compression-injection hybrid system (Toshiba machine co.). A CFRP sheet in fig 4 was heated and deep drawn. In-situ compound chopped carbon fiber reinforced XD10 was injected to form ribs and bolt-holes, simultaneously. It showed good deep drawing and good adhesion between injected resin and resin in CFRP sheet.



Figure 9: A automobile Part Made by Compression-Injection Hybrid System from Toshiba Machine co.

Figure 10 shows pultrusion molding samples using UD Tape and braided commingled yarn. Pultrusion was tested in Gifu University. As a pultrusion molding is superior to productivity and long products, it is under investigation for automotive use.



Figure 10: Pultrusion Molding Samples Made from UD Tape (left) and Commingled Yarn (right).

Figure 11 shows a simulated drone-propeller using tailored fiber placing and light molding system. The commingled yarn was embroidered on a polyamide film by fiber laying machine from Tajima Group. The direction of carbon fiber was exactly controlled by this system. Furthermore, as an embroidering process emits few loss of production, cutting process and material cost can be saved. Finally, the well-placed preform was cured by Amolsys system from D-MEC Ltd. The preform was put into a silicone mold, and then, vacuumed and heated using near-infrared light for impregnation. As resin fibers and carbon fibers were mixed well in a commingled yarn, it is enough to form a fine molded article under (atmospheric pressure). After cooling, the objective was obtained. This method is especially effective for productions of many models in small quantities, because the design of a product can be easily changed by fiber laying method, and the silicone mold for light molding is much more inexpensive than a metal mold, which is usually used for hot press.



Figure 11: Simulated Propeller; Fiber Laying Prepreg (left) from Tajima Group, and Light Molding (right) from D-MEC Ltd.

XD6 and XD10 can be combined to metal and thermosetting CFRP. Figure 12 (left) shows metal/CFRP lamination rod, in which a light bulb is. UD tape was wound on sanded metal pipe, and then, hot pressed. As XD6 and XD10 had good metal adhesion property, they bound together well without using adhesives. Figure 12 (right) shows an oar. The shaft and grip is thermosetting CFRP, and the blade is XD10-CFRTP. They were bonded by epoxy type adherence. As XD6 and XD10 contains amino terminal, they bond strongly to epoxy type adherence as well as thermosetting plastics.



Figure 12: Lamination of XD10-CFRP with Metal, a pipe from SPIC co. (left), and Bonding of XD10-CFRP with Thermosetting CFRP, an oar from Fudow co (right).

Why XD6 and XD10 are useful.

XD6 and XD10 met demands of each prepreg and molding process. It was considered there were three important characters to achieve each process; high degrading temperature, low water gain, and proper rate crystallization. The 5% weight reduction temperatures of XD6 and XD10 (LEXTER 8500) were 383 °C and 392 °C, respectively. Considering their melting temperatures were 237 °C and 213 °C, respectively, they had wide temperature range to control melting viscosity during molding (Fig. 13), because melting viscosity decreased by raising temperature.

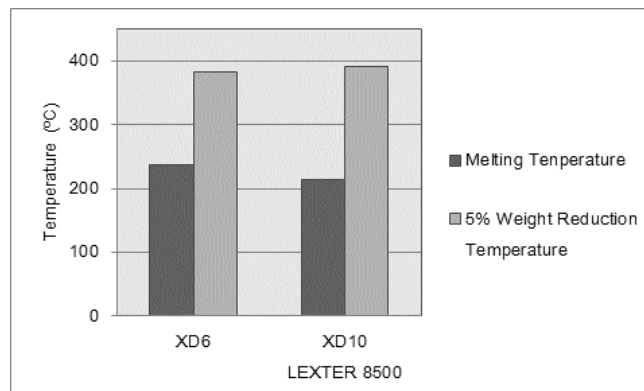


Figure 13: Water Absorption Curves of Polyamide Resins.

Specimens were dipped in water at 23 °C. Water absorption curves were shown in figure 14. Water absorbing ratio of XD6 was slow. That of XD10 was even slower and water content of

XD10 after 600 days remained under 3%. Such a character avoided a trouble of having to water condition control, and allowed better production of prepregs written above. Moreover, they generated less water vapor during molding processes.

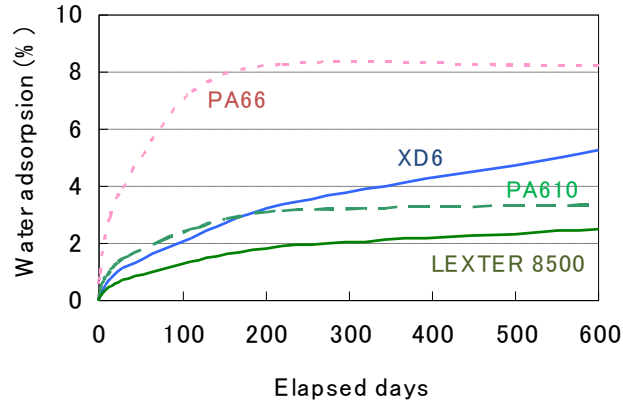


Figure 14: Water Absorption Curves of Polyamide Resins.

Half-times of crystallization⁽⁶⁾ of polyamides were shown in figure 15. Low half-time of crystallization indicates that the crystallization speed is fast. XD6 and LEXTER 8500 seemed to be appropriate crystallization speed. It is fast enough to induce crystallization during molding process, and generate heat hardness and solvent resistance. On the other hand, it is slow enough to finish impregnation, and display a good surface appearance.

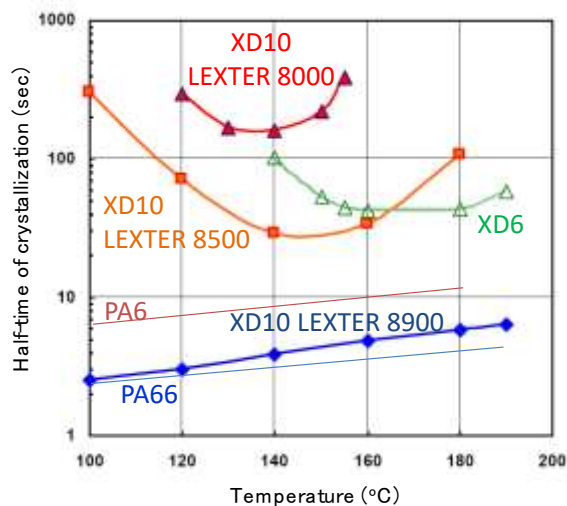


Figure 15: Crystallization Rates of Typical Polyamides.

Summary and Next Steps

Polyamide XD6 and XD10 have excellent mechanical properties. These properties were fully reflected when they were used as matrix resins of FRTP. Their low water content, proper rate crystallization and high thermal stability enabled many types of prepreg fabrications, and FRP molding methods. Next, XD6 and XD10 have to be modified to meet a final product demand such as flame resistance, weather resistance and impact absorption. These problems are under investigation. Finally, I would like to thank companies in collaboration, Prof. Nakai of Gifu University and Prof. Ohtani of KIT University, and Dr. Matsuba and Mr. Nishida from Hiroshima Prefectural Technology Research Institute.

References

1. E.F. Carlston, F.G. Lum, "m-Xylylenediamine Polyamide Resins," *Ind. Eng. Chem.* 49 (8) (1957) 1239-1240.
2. Y.S. Hu, V. Pratiapati, A. Hiltner, E. Baer, S. Mehta, "Improving gas barrier of PET by blending with aromatic polyamides", *Polymer*, 46 (8) (2005) 2685-2698.
3. M. Chanda and S. K. Roy, "Industrial Polymers, Specialty Polymers, and Their Applications", Taylor & Francis Group/CRC Press, New York, 2009.
4. *New Engineering Plastics*, Reny, Mitsubishi Engineering-Plastics Corp., Tokyo, Japan, 1994.
5. A. K. Kaw, Chapter 3 micromechanical analysis of a lamina, "Mechanics of Composite Materials", second edn. CRC Press.
6. J. H. Magill, "A new method for following rapid rates of crystallization I. Poly(hexamethylene adipamide)" *Polymer*, Vol. 2, 1961, pp. 221-233.