

A NOVEL ORGANIC FIBER FOR FIBER REINFORCED STRUCTURAL COMPOSITES

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Abstract

A novel fiber technology is being developed for the fiber reinforced composites industry. The fiber is a form of poly vinyl alcohol (PVOH). When added to conventional fiber reinforced composite PVOH fiber gives exceptional impact resistance, surface finish and improved recycling properties to fiber reinforced composites. PVOH is highly chemical and UV light resistant compared to other commercially available reinforcing fibers. PVOH is also economical compared to many high performance reinforcing fibers. PVOH can be used in combination with existing fibers (such as fiberglass, polyester, Kevlar) or as a stand alone fiber in both thermoset and thermoplastic resins. PVOH requires distinct surface modification to make the fiber compatible with each commercial polymer resin system. PVOH is commercially available for polyester and epoxy resins with vinyl ester, phenolic, polyolefin, silicone and urethane resins in development. Advanced resin systems have been demonstrated that create a bond that is stronger between fiber and resin than the fiber itself, giving a moldable composite with true isotropic properties. PVOH fiber is being targeted toward a broad array of applications and markets. Applications include molding compounds (bulk and sheet), pre-pregs, mats (woven, non-woven and uni-directional), braided structures, and chopped fiber (including wet laid). Markets include aerospace, automotive, construction, consumer, electronics, marine and the chemical industry. PVOH has a fit wherever molded composites require a lightweight reinforcing fiber with excellent impact, chemical and environmental properties.

PVOH History

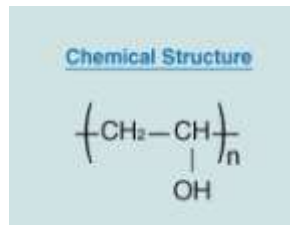
Traditional PVOH is water soluble and has commercial uses in adhesives, mold release agents, primer paints, and as a binder for many products. The PVOH discussed in this paper is hydrophilic and is manufactured as a high modulus fiber with the appearance and feel of a PAN acrylic fiber. High modulus PVOH has been used commercially in textiles, construction materials and the paper industry. PVOH has long history of development in Asia for use in fiber reinforced concrete and roofing shingles. In Japan, PVOH is widely used to reinforce stucco type concrete for commercial and residential buildings. Other long term applications of high modulus PVOH include a 1000 ft span concrete road bridge and the railway cross ties for the Japanese bullet train system. These two applications have over 30 years of in-field data and demonstrate the exceptional environmental stability of PVOH fiber. PVOH has been used to demonstrate "bendable concrete" as part of a research and development program at the University of Michigan¹. The largest supplier of PVOH in Asia is Kuraray with annual production capacity of 40,000 MT. Other producers of high modulus PVOH include Japanese, Korean and Chinese manufacturers that supply the construction industry worldwide. Today Kuraray is the leader in the development of PVOH fiber for FRP reinforced composites applications. PVOH

¹ Li, V.C., T. Horikoshi, A. Ogawa, S. Torigoe and T. Saito, "Micromechanics-based Durability Study of Polyvinyl Alcohol-Engineered Cementitious Composite (PVA-ECC)," *ACI Materials J.*, Vol. 101, No. 3, pp. 242-248, 2004

has been commercialized in applications including; high pressure brake hose and HVAC hose reinforcement; FRP safety helmets; conveyor and V belts; tire cord; and industrial hydraulic hose. Kuraray uses the trade name “Kuralon” for its’ family of PVOH fiber. Because of Kuraray’s long history in PVOH fiber development and their extensive testing database, Kuralon fiber test data is referenced throughout this paper. Future market development is directed toward the 4.11B lb/yr North American market for FRP composites. With initial success developing in the BMC market, product development efforts for PVOH fiber reinforced components are now expanding into a wider array of resins and applications. The principle challenges for adapting PVOH into the present market is two fold. Compatibility with a broader array of resin systems is acknowledged as significant technical challenge. The second challenge is building the supply chain and customer acceptance for products that include PVOH fiber. Unlike many other large scale industries in North America, the composites industry has many smaller scale specialty companies that focus on a particular market niche. Successful market introduction of PVOH fiber will require focused team building that includes choosing the right compounding companies, pre-form makers, resin suppliers and fiber converters to deliver a complete PVOH FRP composite product. PVOH will selectively enter the FRP market where enhanced impact resistance, lighter weight, and surface finish features of PVOH FRP composites create the most value for the customer.

High Modulus PVOH for the North American FRP Market

PVOH is a unique fiber that has performance and economic properties that place PVOH between common organic fibers that are low performance and highly engineered fibers that are expensive. PVOH is a polymer chain with the general chemical structure:



PVOH can be used as a stand alone reinforcing fiber or in combination with other fibers to extend the properties of engineered FRP composites. In combination with fiberglass, PVOH fibers can increase the impact strength compared to fiberglass only FRP composites by a factor of 10. The mechanical properties of PVOH fiber can be varied based on manufacturing technique with a general trade off between elongation vs. tensile strength. The higher the modulus desired in PVOH fiber, the smaller the fiber diameter will be. Chemical, thermal and fiber density properties are constant. PVOH fiber has inherent mechanical stability with a low creep factor and low dry heat shrinkage. PVOH is limited to 400°F for processing into FRP components and should not be held at high temperatures for extended dwell times. Thermal decomposition of PVOH yields mostly water and small percentages of CO and CO₂. Compared to other synthetic and natural fibers, PVOH decomposes with minimal environmental impact. PVOH is produced as either a continuous fiber tow (typically 1000 filaments) or as a cut fiber (38000 filaments chopped) depending on the application and desired performance. PVOH filament fiber can also be post processed to specific cut lengths, have crimps formed, and

incorporate specific surface finishes depending on the type of resin system being used to manufacture FRP components. PVOH is manufactured under tight process controls and high purity standards. General fiber quality can be visually determined by the whiteness of the fiber. Lower performance PVOH fiber will have higher impurities and tend to be yellow in color. The impurities in low quality PVOH fiber adversely affect the mechanical and chemical properties of the finished fiber. Mechanical strength, elongation, water absorption and thermal stability are all negatively affected. The other keys to manufacturing high quality PVOH fiber involve controlling the processes for stabilizing the vinyl alcohol resins and drawing the finished polymer fiber. PVOH fiber properties range as follows:

Commercial PVOH Fiber

Type		1239	1225-7	1203-2	5501	5506	5508-1	5516-1
Thickness	dtex	1330	1100	1330	2000	1330	1100	2000
Number of filament		200	200	200	1000	600	600	1000
Breaking strength	N	110	78	90	196	128	105	238
Tenacity	cN/dtex	8.2	7.1	6.8	9.8	9.6	9.5	11.9
	g/dr	9.3	8.0	7.7	11.1	10.9	10.8	13.5
	GPa	1.06	0.93	0.88	1.27	1.25	1.23	1.55
Elongation at break	%	7.7	10.0	13.5	6.6	8.0	9.0	6.4
Young's modulus	cN/dtex	177	159	137	203	177	168	260
	GPa	23.0	20.7	17.8	26.4	23.0	21.8	33.8
Dry heat shrinkage (at 160°C for 30min)	%	0.8	0.8	0.8	0.6	0.6	0.4	0.4
Boiling shrinkage (at 100°C for 30min)	%	4.5	4.5	4.5	2.5	2.5	2.0	2.2
Specific gravity		1.30						
Melting point	°C	over 240						
Commercial moisture regain	%	5.0						

This a partial list of the spectrum of filament fibers that can be produced in commercial volumes.

Mechanical Properties of High Modulus PVOH

Comparing PVOH filament fiber to other commercially available reinforcing fibers reveals that PVOH fiber has properties that place it in a unique place in the market. The overall properties of PVOH fiber (mechanical, chemical, weatherability and dimensional stability) compare favorably to competing fiber technologies as follows:

Fiber Mechanical Properties Comparison

Fiber:	Glass	PET	Rayon	Polyester	Nylon-6	Aramid	Kuralon*
Young's Modulus [cN/dtex]	198	193	86	110	34	493	274
Tenacity [cN/dtex]	4.4	7.9	4.7	7.8	8.1	19.4	11.2
Elongation at break [%]	2.0	16.6	11.9	11.9	19.4	3.9	6.9
Fiber Diameter [microns]	13	21	12	10	10	12	14
Specific Gravity [g/cc]	2.54	1.38	1.52	1.38	1.14	1.41	1.30

* Kuraray 5516-2 PVOH filament fiber

PVOH has the best balance of mechanical performance and fiber weight when compared to conventional fiber technologies. Compared to Aramid fiber, PVOH is less than 20% of the cost by weight for equivalent fiber loading in FRP composites.

Long Fiber (LFT) Properties of PVOH FRP Composites

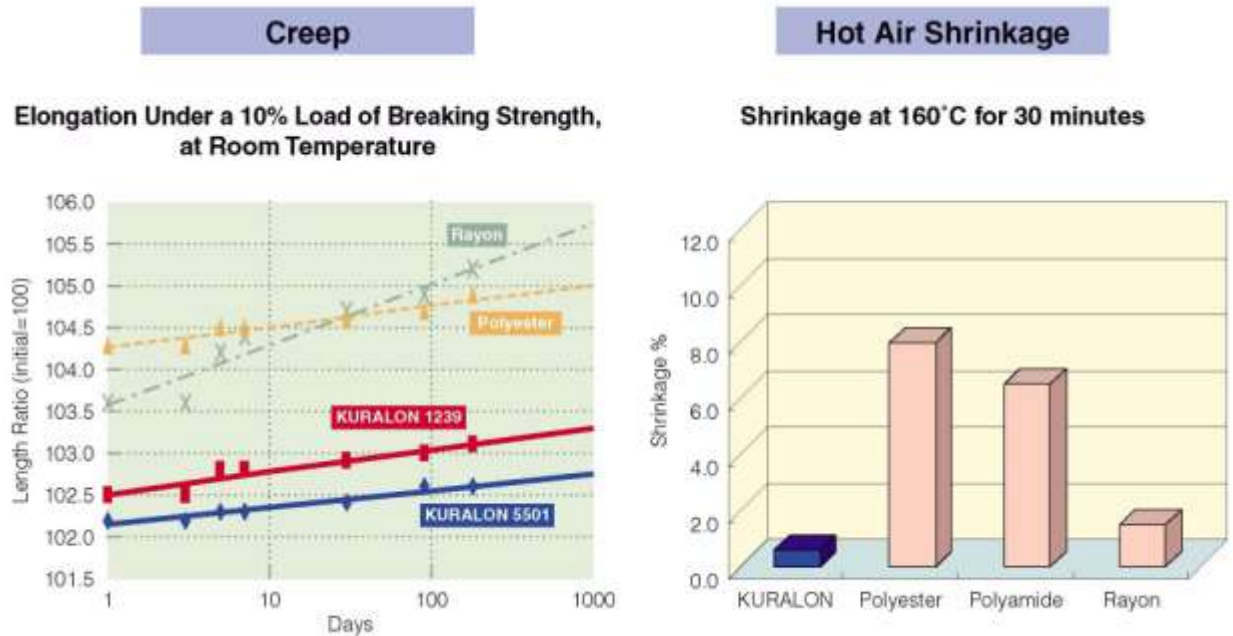
PVOH in chopped fiber form has excellent retention of fiber length which contributes to the impact resistance of FRP composites that incorporate PVOH fiber. Impact tests conducted using fiberglass or PVOH fiber equally loaded in polyester resin plaques resulted in significantly greater impact resistance for the PVOH fiber plaques. Using a vertical steel ball drop test onto a 10% fiber loaded plaque, the plaque containing fiberglass only failed from a 10cm drop. The equally loaded PVOH fiber plaque failed from a 100cm drop. For a second set of tests in thermoplastic resins, polypropylene coupons were prepared with various fibers and fillers to demonstrate the improvement in mechanical properties by incorporating PVOH fiber. The test results are shown below:

Properties of PVOH Fiber in Polypropylene Thermoplastics

Fiber & Mica Content	Charpy Impact Strength (Kj/m ²)	Flexural Strength (N/mm ²)	Flexural Modulus (N/mm ²)	Tensile Strength (N)	Tensile Strength (N/mm ²)
Fiberglass 20%	15.0	35.0	2743.0	954.9	31.4
PET 10%	24.1	27.4	972.9	647.6	21.3
Vectran 10%	45.7	35.6	1408.0	1077.2	35.5
PVOH 10%	36.4	31.4	1325.9	937.7	30.9
PVOH 5% Mica 2%	21.9	30.6	1320.2	765.5	25.2
PVOH 10% Mica 14%	34.0	38.9	2467.4	972.6	32.0
Control (100% PP)	14.1	27.9	999.6	720.7	23.7

There are many potential combinations of PVOH and other fibers or fillers that will yield the specific combinations of properties desired for a FRP composite application. The example above demonstrates that stiffness doesn't need to be reduced in order to achieve improved impact resistance.

Dimensional Stability



PVOH fiber elongates less than 0.5% after 1 year under continuous load. PVOH thermal shrink back is minimal and will not shrink back during molding process, yielding improved composite part finish.

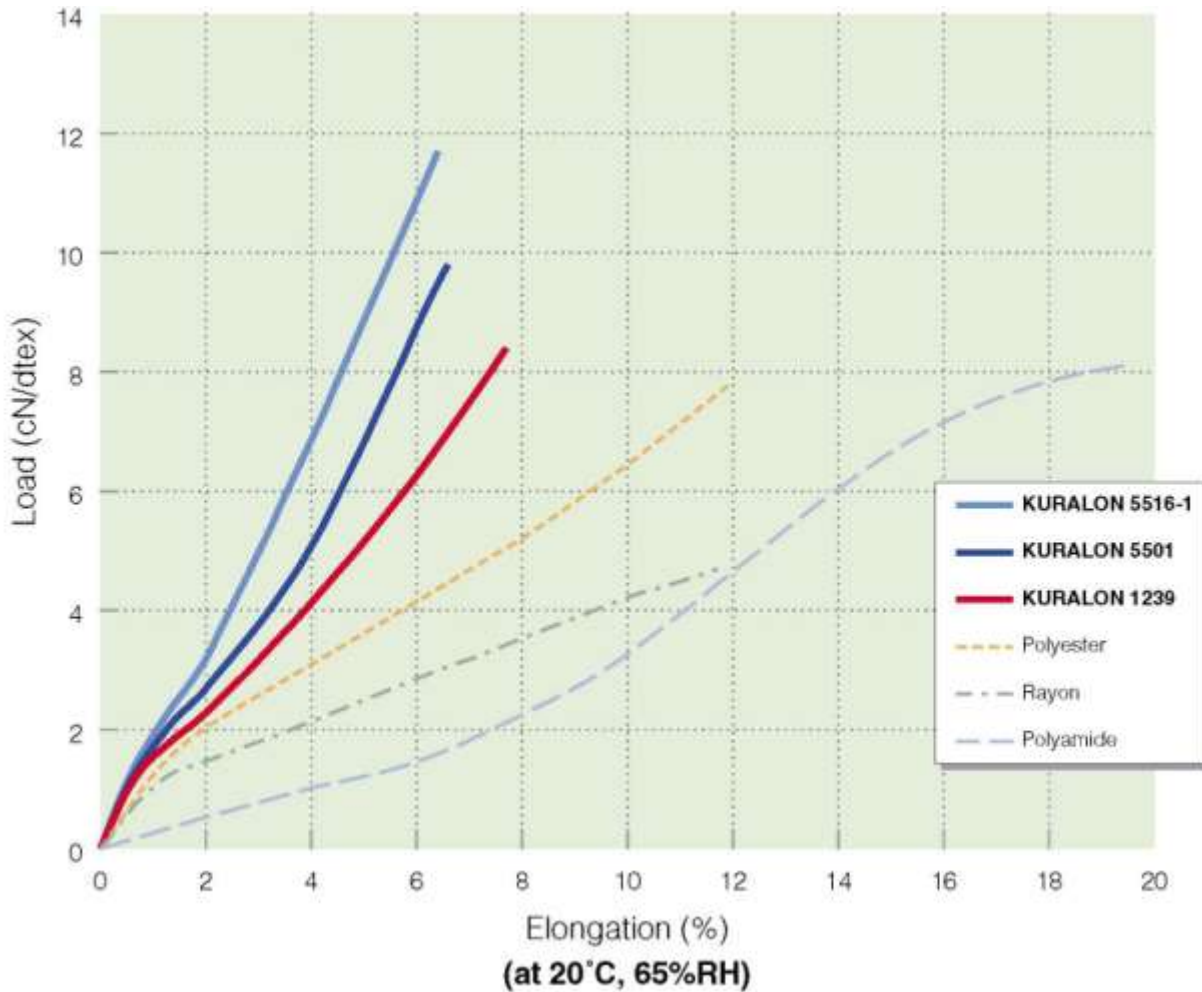
PVOH Refractive Index to Visible Light

Visible-Light Refractive Index of Selected Synthetic Resins

<u>Resins</u>	<u>Refractive Index</u>
Polyester Resin	1.53 – 1.57
Urea Resin	1.54 – 1.56
Vinyl Chloride Resin	1.52 – 1.53
Polyethylene Resin	1.51
Methacrylic Acid Resin	1.48 – 1.50
Silicone Resin	1.47 – 1.49
Nylon Resin	1.53 – 1.57
Glass Fiber	1.548
<i>Kuralon Fiber</i>	1.520 – 1.562

When PVOH fiber reinforced composites have been resin-impregnated, the refractive index of the PVOH fiber allows for the highest possible transparency of the FRP composite (depending on the resin system). PVOH fiber readily accepts coloration and yields a resin rich surface in molded composites.

Load vs. Elongation Performance



PVOH fiber demonstrates mechanical properties that compare favorably with all reinforcing fibers whether the measure is strength, elongation, modulus, light transmission, thermal stability, creep, shrinkage or weight. PVOH can improve the mechanical properties of a wide range of FRP products by replacing or supplementing the fiber technology presently in use. In addition to the excellent overall mechanical properties of PVOH fiber, PVOH has superior environmental and chemical performance to a wide range of fiber technologies in use today.

Chemical and Environmental Stability of PVOH Fiber

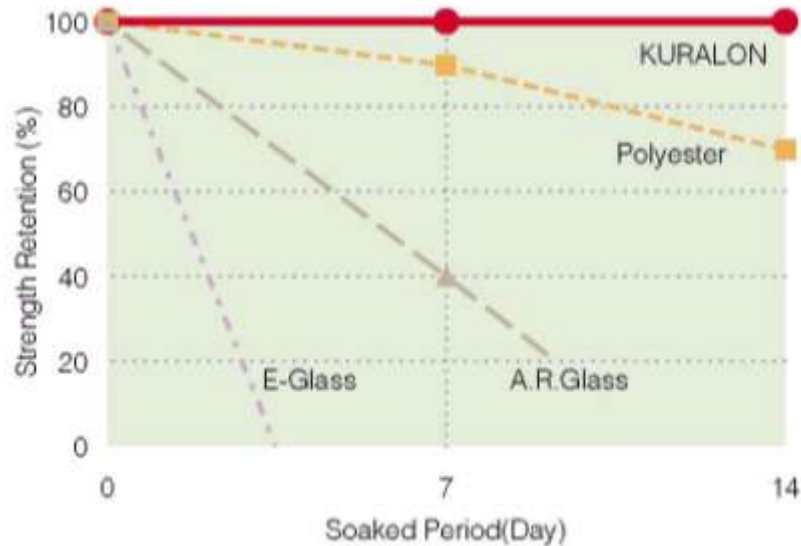
Because of its chemical structure PVOH fiber has exceptional chemical stability and weatherability. PVOH fiber is extremely stable in alkalis, salts, oils and common acids, all the chemicals typically found in automotive and marine applications. FRP composites using PVOH and a corresponding resin system can be applied to extreme chemical environments where other fiber systems would fail. PVOH fiber chemical stability is shown below:

PVOH Comparative Chemical Stability

Chemicals		Test condition			Strength retention			
		Conc.	Temp.	Time	KURALON	Polyester	Polyamide	Rayon
		%	°C	hrs.	%	%	%	%
Acids	Sulphuric acid	1	20	10	100	100	97	84
		10	20	10	100	100	56	55
	Hydrochloric acid	10	20	1	100	100	76	83
		10	20	10	100	95	77	69
	Nitric acid	10	20	10	100	100	86	90
Alkalis	Sodium hydroxide	1	100	100	100	29	75	71
		40	20	10	100	97	82	0
Salts	Sodium carbonate	1	100	10	97	95	99	85
	Sodium chloride	3	100	10	100	100	84	98
	Ferric chloride	3	100	10	89	100	55	0
Organic solvents	Aceton	100	20	1000	99	100	88	100
	Benzene	100	20	1000	100	93	88	90
Oils	Mineral oil	100	100	10	100	100	100	10
	Linseed oil	100	20	1000	100	93	92	100

Given the chemical stability of PVOH fiber in alkali environments, the largest commercial application today for high modulus PVOH fiber is fiber reinforced cement. PVOH was chosen by the construction industry to systematically replace asbestos fiber in concrete applications. PVOH is also ideal for battery separator materials in NiMH and NiCad batteries. Comparative data is shown below:

PVOH Alkali Resistance*



* In cement water @ 80°C under load

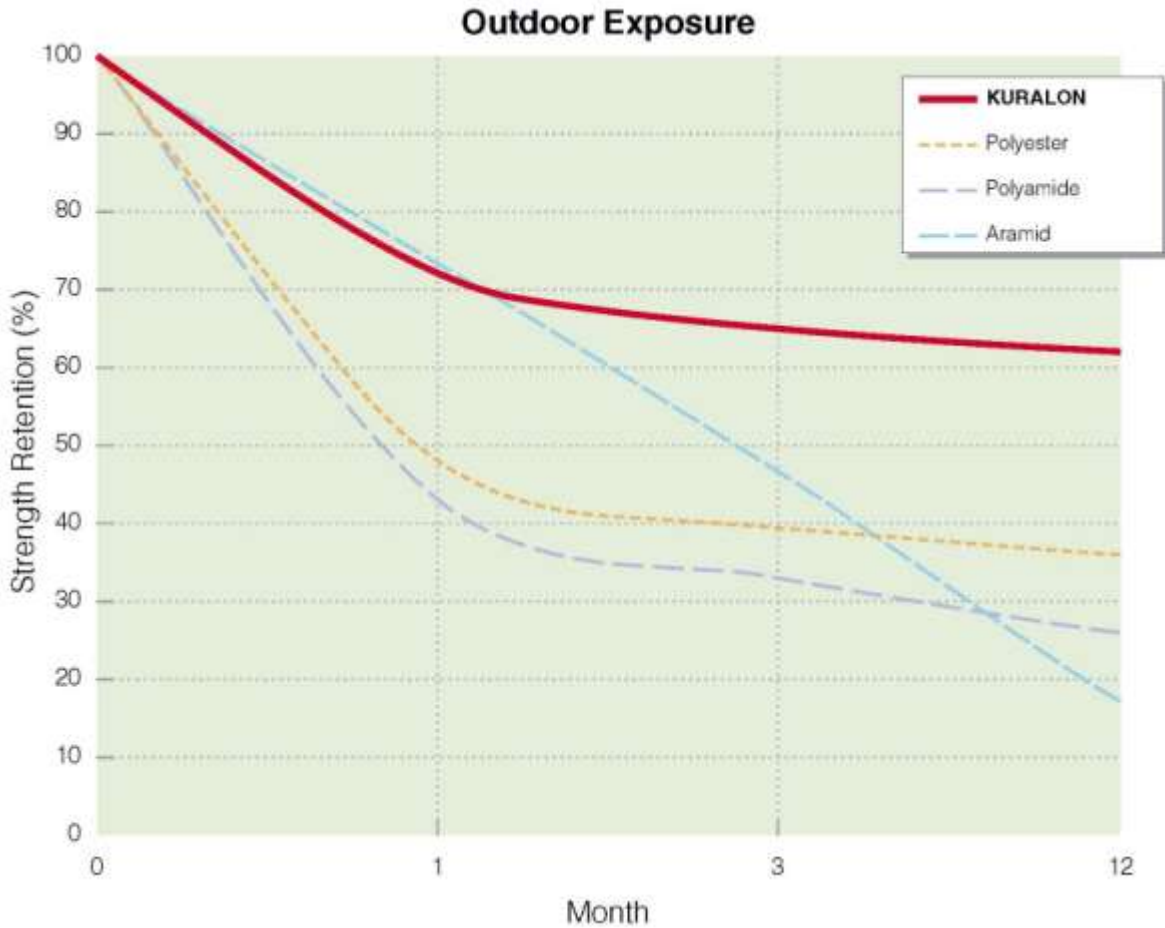
Many engineered organic fibers are susceptible to ultraviolet (UV) radiation degradation. PVOH fiber is exceptionally stable in conditions of prolonged UV exposure. Many applications for FRP composites expose the materials to prolonged exposure to UV radiation. Automotive interiors, Marine structures, construction materials and aerospace composites are just a few of the markets where UV degradation is a consideration in designing FRP composites. The following chart compares PVOH fiber to selected commercial organic fibers:

PVOH fiber strength retention stabilizes after prolonged UV exposure. Other high performance fibers that have higher modulus initially never stabilize and after extended exposure to UV radiation retain less strength than PVOH fiber.

Environmental Attributes of PVOH Fiber

PVOH resins (the building blocks for PVOH fiber) has been determined to be safe for use in the production, processing and packaging of food. PVOH has the approval of the Food and Drug Administration (USFDA). There are many products that use PVOH films as barrier materials for sale today. PVOH has been developed for applications that range from contact lenses to coatings for implantable medical devices. For FRP composite applications PVOH fiber provides an organic component with excellent disposal properties. During thermal decomposition PVOH yields nearly 99% water vapor (by weight) and heat. Only 0.45% CO gas is produced. Other synthetic and natural fibers produce ammonia (NH₃), cyanide (HCN), and hydrogen sulfide (H₂S) during thermal decomposition. Fiberglass cannot practically be thermally decomposed and must be handled separately after the organic component of a FRP composite has been removed. By comparison, PVOH (Kuralon) yields little environmental contamination (see below):

UV Weatherability of PVOH Fiber



Comparison of By-Products from Thermal Decomposition

	CO	CO ₂	NH ₃	HCN	H ₂ S
KURALON	0.45	0.59	—	—	—
PAN	1.33	0.15	0.06	0.09	—
Polyamide	0.88	0.40	0.05	0.03	—
Cotton	4.33	0.75	—	—	—
Wool	2.00	0.59	0.10	0.05	0.04

*Sample weight: 10mg

The figures above are percentages by weight of the residual gasses generated during thermal decomposition of 10mg samples at 600°C.

PVOH has the added property of no flame propagation. In the presence of a flame, PVOH will shrink away rather than burn.

Advancements in PVOH High Modulus Fiber

The next steps for PVOH fiber are two fold. The first goal is to develop commercial applications for PVOH to introduce the fiber to the North American market. PVOH fiber is moving forward in the FRP composites market with a selected group of commercial developers. PVOH is under test at seven companies for applications that include bulk molding compounds, sheet molding compounds, liquid molding compounds, uni-directional pre-pregs, push-trusion compounding, long fiber molding pellets and braided reinforcements. With first generation polyester and epoxy resin finishes available, PVOH fiber has begun entering the marketplace in thermoset molding compounds. PVOH will enter the commercial market in 2006. The second goal for PVOH is to reduce the number of fiber types offered to the market and expand the number of fiber finishes available to support a wider variety of resins. Today, Kuraray manufactures 12XX, 55XX, and 79XX series PVOH fiber. For the FRP composite market, 55XX fiber has been chosen as having the most suitable mechanical properties and economics. By simplifying the choices in fiber the economics of volume production will be achieved quicker and production can be established locally. Wide arrays of fiber finishes are in development to support the most commonly produced resins. This allows for a broad array of FRP composite applications to adopt PVOH reinforcement fiber. PVOH is not strictly intended to be a replacement for fiberglass. PVOH is designed to enhance the properties of many commercial molding compounds available today as well as create new products from the unique properties PVOH gives to FRP composites. To borrow an advertising phrase from BASF, "We don't make the product, we make the product better!"