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Polymers

Polyvinylidene fluoride fibres for multiple high performance uses

Polyvinylidene fluoride (PVDF) has long been used for industrial monofilament applications. In this article for *Filtration+Separation* Sean M Stabler, James Henry, and Jerome Chauveau of Arkema, developers of the new Kynar PVDF, discuss how fresh grades allow the dimensions of fibres to be scaled down to very low diameter fibres, giving access to new opportunities. They state it is an adaptable fluoropolymer, whioh can be applied to many markets including transportation and chemical processing.

Kynar PVDF is available as a homopolymer or copolymer resin especially designed to be manufactured into mono and multi filament fibres to be converted into woven and nonwoven articles.

Polyvinylidene fluoride (PVDF) is a high performance engineering polymer which was introduced in the 1960s when Arkema began manufacturing the trademarked Kynar PVDF family of materials. Today, there are more than 40 different Kynar PVDF grades available to the market for a wide range of manufacturing processes including extrusion, injection moulding, rotational moulding, coatings, and solution casting. The ease of processing has led to applications which include: corrosion resistant liners for tanks and pipes; protective films for photovoltaic solar panels; barrier films for bioprocess and pharmaceutical disposable systems; high purity components for semiconductor water and chemical processing; flame and smoke resistant wire and cable jacketing for plenum rated products; protective paints for architectural coatings; membranes for filtration of water and food; foams for light weight applications; and most recently fibres for woven and nonwoven applications [1,2,3,4,5].

Background

Terminology often associated with the traditional polymer industry is quite different than that used for the fibre industry. It is important to note a key term and how it relates to specific polymers and the design of components made from said polymers.

Denier is simply the term used to describe the mass per unit length of a linear material. For fibres, denier is defined as grams per 9,000m of fibre. Specific gravity is the unit mass per volume. Relatively speaking, Kynar PVDF material is considered to be a high density material as compared to common synthetic fibre materials such as polypropylene and polyester. As such, density should be considered when comparing denier per filament (dpf) of

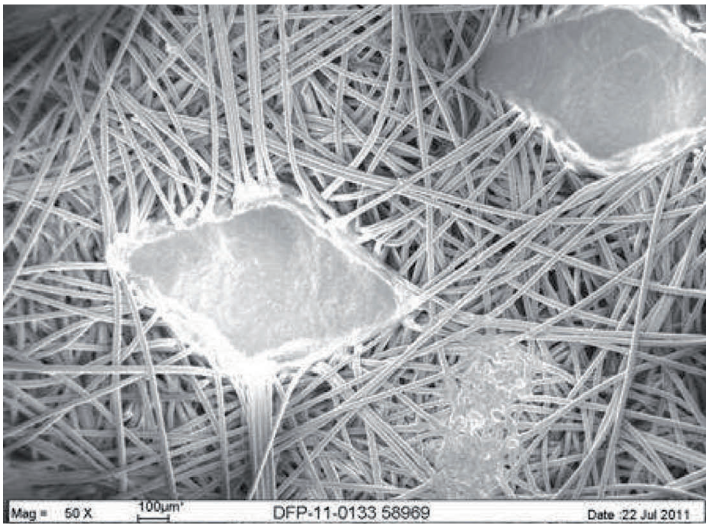

Figure 1: Kynar nonwoven point bonded.

Figure 2: Kynar crimped multifilament.

different polymers. Table 1 below shows how the specific gravity has an effect on the fibre diameter as compared to a constant denier per filament.

For example, it is important to note that when specifying a 3dpf of PP and PVDF, one should understand that the fibre diameter of PP is 29% larger, which can have a significant effect on the final products performance. With this noted smaller diameter fibres lead to higher specific surface areas in filters, as the specific surface area varies inversely with diameter (~1/d)[6]. So it is important to understand how the specific gravity of a synthetic fibre has an effect on fibre diameter for a constant denier per filament. This is especially important for filtration, as surface area of fibres is a key variable to filtration efficiency.

General properties of PVDF

To fully understand why there is a growing interest in Kynar PVDF fibres; let's discuss some of the key attributes of this versatile fluoropolymer.

Kynar PVDF is an adaptable fluoropolymer, finding applications in many markets including chemical processing, electricity and electronics, high purity, transportation, and architecture. Some of the key attributes of Kynar products, without additives or post treatments, is naturally:

- hydrophobic[4]
- oleophobic[4]
- abrasion resistance
- flame resistance – high LOI
- chemically inert
- up to 150°C use temperature
- triboelectric
- high thermo-mechanical strength
- 'weatherable' – especially to UV
- low coefficient of friction
- resistant to fungal growth
- oxidation resistance
- high crystallinity

Polymer	Specific Gravity (g/cc)	Denier/ Filament (dpf)	Fiber Diameter (micron)
PTFE	2.15	3	14.1
PVDF	1.78	3	15.4
Polyester	1.38	3	17.6
PP	0.905	3	21.7
PPS	1.35	3	17.8

Table 1: Comparison of polymers for fibre.

Kynar Grade	Melt Temperature (°C)	Melt Viscosity (kpoise)	Typical Fiber Diameter (mil)
705	168	2-4	<<10
710	168	4-8	~10
720	168	6-12	10-40
740	168	15-22	20-125
760	168	23-30	20-125
460	160	23-29	20-125

Table 2: Standard Kynar fibre grades.

Kynar PVDF has excellent chemical resistance and is often specified for applications due to total resistance to:

- water – including steam
- strong acids
- strong oxidants
- aromatic solvents
- aliphatic solvents
- hydrocarbons

Kynar products are also used in other chemical applications, but with certain limitations to:

- ketones
- amines
- strong bases
- fuming acids

Of course, all applications are dependent on concentrations, temperatures, pressures, and exposure time.

Another key property of growing interest is its oxidative resistance to both concentrated ozone as well as oxidizing agents. For example, Kynar 705 multifilament fibres having a 1 micron fibre diameter has been fully submerged in 80°C concentrated chromic acid for two weeks. Testing before and after exposure showed no loss in tensile and elongation properties of the fibres. This property is important to both battery applications and water related applications where ozone is commonly used as a sterilisation technique. In addition to sterilisation, Kynar products are safely autoclaved, gamma irradiated, and chemically sterilised.

Similar immersion tests have been performed on Kynar PVDF homopolymer and copolymer products with acetic acid, nitric acid, hydrofluoric acid, sulphuric acid, hydrochloric acid, sodium hydroxide, bromine, iodine, acetone, ethylene glycol, and others with minimal to zero loss in tensile properties. So it is easy to see that a Kynar PVDF fibre could find applications in environments which other polymers could not perform easily or for a suitable duration.

Kynar PVDF's broad range of properties and processability ideally complement its high purity nature as it does not require processing aides like plasticizers and flow aides, nor does it need performance enhancers such as UV stabilizers and anti-oxidants. This attributes to why PVDF grades have an impressive listing of regulatory approvals ranging from USP class VI, NSF 61, ASTM E84, FDA compliant for food contact, etc. For further information on the listing, please contact Arkema Inc.

Kynar resin grades

Fibres are available in many different forms including: staple fibres, nonwovens, monofilaments and multifilaments. These forms are often converted into woven fabrics, knitted fabrics, spun yarns, or nonwovens. Until recently, PVDF has only been available commercially as a monofilament.

Kynar PVDF monofilaments have been used for many years to make fishing line and nets as well as woven fabric cloths used in the bleaching segment of pulp and paper mills[7]. These types of fabrics are generally made from thick monofilament, ~10 mil and greater. The monofilament products can be produced using several different homopolymer grades of Kynar PVDF resins. The grade typically depends on the melt processing technology of the manufacturer and desired physical properties of the final product.

Arkema has realised that there are a broad range of practices to make Kynar PVDF fibre and have such commercialized several different grades of Kynar PVDF suitable to make melt spun fibres, as shown in Table 2. These same grades, as well as select copolymer Kynar PVDF grades, have also been solvated with known active solvents so that they can be drawn into fibres using electro-spinning and other specialised solution cast technologies[8].

Figure 3. Kynar staple fibre.

The solution spun fibres of these grades have been known to reach <350 nm Kynar fibre diameters.

Until recently, most Kynar PVDF fibres were 10mm and greater in diameter. Arkema recognised that smaller diameter fibres were needed to enter into new markets and applications. So Arkema developed a new homopolymer grade called Kynar 705 which is designed to address the demands of a low diameter fibre. This new grade has been found useful for making micron and even submicron diameter fibres by means of solution or melt spinning practices and has now been used to make other fibre forms including staple fibres, spunbond nonwovens, island and sea fibres, and multifilaments.

The extension of the Kynar PVDF product line has now begun to open the doors for improvements in technologies and developing market opportunities which were not available several years ago. The extension of the product line now allows Kynar PVDF to be manufactured into many major forms of fibres.

Fibre applications

Specific applications of interests for the high flow Kynar 705 grade are fine diameter melt or solution spun processes for conversion into mono and multifilament fibres. These fibres can then be converted into various yarns or fabrics, which can further be manufactured into textiles and filtres.

These woven products can be used in combinations with multifilament fibres of small diameter and monofilament fibres of larger diameter. The larger monofilaments serve as support, while the smaller multifilament fibres increase surface area for improved filtration characteristics. Applications for fibre products are for, but not limited to, liquid filtration of hot acids, oils, water, chlorinated water, suspended solids, 'sticky' materials, etc. Kynar PVDF fibres can also be used for steam and air filters which may have chemical mists from oils, glycols, water, etc.

Kynar PVDF is an excellent polymer for pressurised filters which produce a cake of foulants. Since Kynar PVDF has a low co-efficient of friction, the foulants tend to release from the fibres very easily and can be collected and removed from the systems or easily discharged by back flushing and reverse pressure pulsing. Some of the particles being filtered out can be quite coarse; Kynar PVDF is known for its excellent abrasion resistance and is an excellent choice for these harsh applications.

Multifilament Kynar PVDF fibres can be cut and crimped into staple fibres. The advantage here is that these staple fibres can be converted into a nonwoven by needle punch, hydro entangled, or other means to mechanically form a bound web to form a fabric useful for air or liquid filtration. Staple fibres can further be used in conjunction with other synthetic polymer or glass materials for desired benefits.

For example, Kynar 705 multifilaments can be spun and precision cut into staple fibres for conversion into air, wet, or dry laid nonwovens. These Kynar 705 cut fibres can be incorporated into filters for fuel due to its excellent resistance to hydrocarbons, and fuels containing alcohols like ethanol and methanol. Filters can also be manufactured for diesel and biodiesel fuels as well. Kynar PVDF is extremely resistant to diesel and biodiesel fuels and such would be an interesting solution to the replacement of glass fibres currently used for coalescing filters.

Beyond filtration, Kynar fibres would likely be useful as a barrier material for corrosive environments for example in fibre glass reinforced (FRP) tanks and piping systems, where the nonwovens are incorporated in the FRP matrix to serve as barrier layer when used in harsh conditions.

In addition, Kynar fibres could be useful in areas requiring flame resistance, such as the automotive industry, protective fabrics and garments, etc which would benefit from a material with a naturally high limiting oxygen index (LOI) of 70% without the need of additives or post-treatments to increase the LOI. Other areas may include specialty applications in automotive, aviation and institutional applications where improved flame resistance is often desired.

There are also several applications of interest for textiles. Kynar PVDF fibres are easily woven and can be incorporated with other organic fibres to improve water, chemical or flame resistance of textile fabrics which could be used for shirts, suits, pants, or other accessories which may require low coefficient of friction between the textile and object being covered. Kynar PVDF is also known for its lack of odour absorption and stain resistance, which could likely be valuable for certain garments. Another group of markets for Kynar PVDF fibres are outdoor applications including:

- tents – military and civilian
- awnings
- umbrellas
- flags

Figure 4: Kynar multi-filament spool.

- sails
- geomembranes

The excellent UV resistance of Kynar PVDF has been proven in the paint and solar energy industry for over 45 years and this performance would translate to textile fibres.

There are also several niche markets which Kynar PVDF is an excellent material choice. Perhaps one of the most innovative markets is for battery applications[9]. Kynar PVDF is commercially used as a binder in lithium-ion batteries for the consumer electronic markets because of its excellent oxidative resistance properties[8]. The chemical stability has also gained interests for using Kynar fibres as battery membrane separators. The fibre separators are used to keep positive and negative electrodes apart while allowing transport of ionic charge carriers in electro chemical cells. The chemical resistance and long term durability of Kynar PVDF for lithium ion battery has created great interests in the anode and the cathode section of the battery and now technology is trending towards better separator materials and/or membranes with improved oxidative properties – where Kynar fibres is likely a solution.

Kynar resins have been actively used for microporous ultra and micro filtration membranes for decades. Kynar PVDF fibres can further be used as a complimentary membrane filtration support for food and water. In particular, a great deal of interest is in Kynar PVDF nonwoven technologies. As the fibres continue to reach lower nanometer diameters, the filtration efficiency is improved tremendously. The majority of the liquid filtration markets use harsh chemical agents such as chlorines, bromines, alcohols, acids, ozone, etc. to clean the filtration systems. Kynar PVDF is known for resistance to all of these cleaning and/or sterilisation techniques.

Kynar PVDF monofilaments have been used in pulp & paper and fishing markets for many years. By market demand, Arkema has now developed appropriate Kynar PVDF grades to address new opportunities and applications where a lower diameter fibre product is desired for liquid & air filtration, flat sheet membrane supports, woven textiles, battery separators, personal protective fabrics, flame barrier, and chemical resistant barriers.

Manufacturing Processes

Last, and potentially most importantly, Kynar PVDF parts can be manufactured on standard melt processing equipment by many processing techniques. Kynar PVDF fluoropolymer is easily melt processable. From the perspective of a polymer resin converter, it is very important that standard melt processing equipment can be used to make a broad range of products. Many fluoropolymers require melt processing equipment with specialised corrosion resistant steel and very high temperature capabilities. As a fluoropolymer, Kynar PVDF is an exception as it does not require a special metal alloy extruder, barrel, or screw for melt processing nor does it require high temperature capabilities. Standard melt processing equipment used for polyolefins and other commodity resins is all that is necessary. Whereas, other fluoropolymers, such as FEP, ETFE, ECTFE, PTFE, etc. do require specialised processing equipment and techniques to manufacture into products. These specialised processes and equipment contribute to higher costs for the final product.

Kynar PVDF can also be produced by solution casting and spinning. There are very few solvents which will dissolve Kynar PVDF, the most common are listed in Table 3. Specific grades of Kynar PVDF and solvents have different interactions with each other. See Tables 4 and 5 for a comparison of solution viscosity versus solids content in different solvents.

Solution viscosity information is important for solvent spinning of Kynar PVDF fibres.

In addition to being processable, Kynar PVDF also has another important property. Kynar PVDF is easily welded and thermoformed. Many polymers cannot easily be welded, but Kynar PVDF is known for high strength thermal welds. Kynar PVDF can be thermally formed into shapes by the use of heat. For example, a Kynar PVDF filter could easily be thermally welded from a flat sheet into a tubular structure simply using heat. This is advantageous for assembly and design of filters which may require geometries beyond flat sheet, such as a pleated design.

Solvent	Boiling Point (°C)	Flash Point (°C)
Dimethyl Acetamide	166	70
N-Methyle-2-Pyrrolidone	202	95
Dimethyl Formamide	153	67
Dimethyl Sulfoxide	189	35
Triethyl Phosphate	215	116
Tetramethyl Urea	177	65

Table 3: Active Kynar PVDF Solvents.

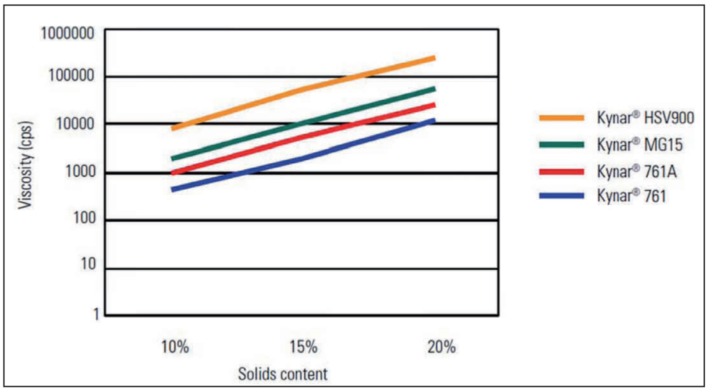

Table 4: Kynar PVDF solution viscosities in NMP.

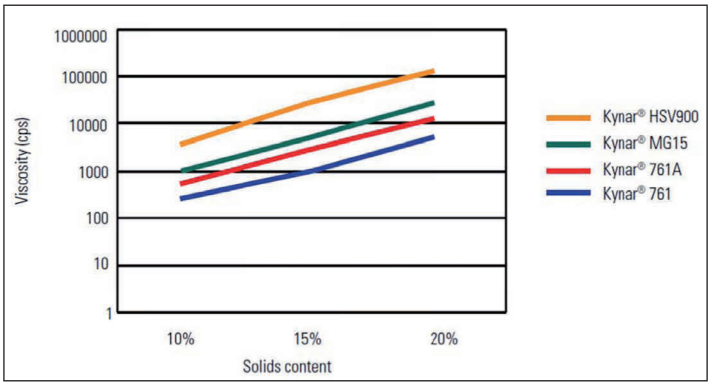

Table 5: Kynar PVDF Solutions in DMAc.

Conclusion

Kynar PVDF is a high performance polymer with versatile properties allowing it to be used in the harshest conditions. The processability of the polymer allows it to take many general forms from pipe to coatings and now to low diameter fibres. As the grades of Kynar PVDF continue to evolve, so will the applications and final products. For more information, contact this paper's authors.

References

Please contact the authors for a complete list of references.

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