

Low Shrinkage in Wire and Cable Extrusion and the Importance of Grade Selection

James J. Henry, Nafaa Mekhilef

Arkema Inc.

King of Prussia, PA 19406

610-878-6023 · james.henry@arkemagroup.com

Abstract

It is widely understood that post extrusion shrinkage can cause problems with the production of Fiber Optic Cables (FOCs). In loose tube and tight buffered fiber optic cables, post extrusion shrinkage may lead to stresses being applied on the optical fiber with the negative consequence of increased fiber attenuation. Manufacturers of fiber optic cables address this problem through proper selection of polymer grades and by optimizing the processing conditions used during cable manufacture. This paper discusses PVDF grade selection as well as specific processing conditions that can be used to minimize post extrusion shrinkage with the goal of reducing its negative consequence on fiber attenuation. Tooling selection, processing conditions and polymer characteristics that minimize polymer orientation and reduce post extrusion shrinkage will be discussed. Much of what is presented in this paper can also be applied to other materials commonly found in fiber optic applications.

Keywords: PVDF, Kynar®, Shrinkage, Shrinkback, Optical Fiber Cable, Excess Fiber Length, fiber attenuation

1. Introduction

Poly(vinylidene fluoride) (PVDF) is an engineering resin obtained by the free radical polymerization of 1,1-difluoroethene (or vinylidene fluoride) (VDF or VF₂) having a chemical structure of $-\text{[CH}_2\text{-CF}_2\text{]}_n-$. PVDF homopolymers are highly crystalline and characterized by a relatively high flexural modulus compared to other fluoropolymers. PVDF is often times copolymerized with hexafluoropropylene (HFP), chloro-trifluoroethylene (CTFE) and/or tetra-fluoroethylene (TFE) to modify its physical and mechanical properties [1]. Incorporation of comonomers reduces crystallinity, which lowers the flexural modulus and increases elastomeric properties. Besides variations in comonomer type and content, commercially available PVDF grades are provided in a variety of viscosities allowing use in various melt processing applications. Higher viscosity products are suitable for many extrusion processes in the production of sheet and pipe. Lower viscosity products are commonly used for injection molding, tubing and the majority of wire & cable jacket and insulation applications.

PVDF polymers, like other fluoropolymers, are very resistant to burning and inherently have low smoke generation characteristics. The unmodified resins have a high limited oxygen index (LOI) of 43 and are rated V-0 per UL94 [2]. Special low flame and smoke grades of PVDF that incorporate flame retardant additives (increasing the LOI up to 100) are commercially available. Low flame and smoke PVDF products are commonly used for the production of plenum cables installed in air handling spaces of commercial buildings. Plenum cables require exceptionally low flame and smoke properties in the event of a fire. This is easily

met using a variety of PVDF grades. The unique set of properties provided by PVDF polymers makes it the preferred material for high-end cable jackets in applications requiring superior flame and smoke properties.

PVDF is most commonly used as a jacket for cable products and is applied using an extrusion process referred to as tube or “Tube-on” extrusion. Jacket extrusion typically runs at high line speeds ranging between a few hundred feet per minute to over 1000 feet per minute. The shear environment through a wire extrusion die can be fairly high and will produce polymer orientation in the extrudate. More importantly, the melt is drawn at moderate draw down ratios (DDR) outside of the die in a manner that introduces considerable polymer orientation. A draw down ratio of 7 to 1 is typical for PVDF jacket applications, although higher and lower DDR is often used. The act of drawing the extrudate outside the die produces a considerable amount of molecular orientation that is often times frozen in as the extrudate freezes. It is the act of drawing the polymer outside the die followed by quench cooling that causes the majority of polymer alignment resulting in jacket shrinkage [3]. Shrinkage of the jacket, commonly referred to as “shrinkback”, occurs as this frozen-in polymer orientation relaxes in the solid state.

In this paper, we discuss the effects of polymer orientation on post extrusion shrinkage. It is widely understood that post extrusion shrinkage can cause problems in cable products, most notably with the production of FOCs. Post extrusion shrinkage of jackets or buffer tubes used in FOCs can lead to Excess Fiber Length (EFL), which is described as the ratio of fiber length to actual tube length. EFL can introduce stress on the optical fibers resulting in signal loss. Post extrusion shrinkage is commonly referred to as “shrinkback”, and we will use this term through the remainder of this paper to describe this behavior. Actions taken to reduce frozen in orientation will result in a reduction in shrinkback and EFL. These actions include process optimization and the correct selection of PVDF grades.

2. Low Shrinkage in Wire and Cable Extrusion

The effects of processing conditions on shrinkback can sometimes be considerable and much effort is placed on finding conditions that minimize these effects. As a general rule, any process modification that reduces the amount of extensional deformation (stretching) of the polymer can potentially reduce shrinkback. A reduction in the draw down ratio can be a good first step to reduce shrinkback. PVDF resins are typically processed using tip/die combinations that will produce a draw down ratio nominally at 7 to 1. Lower draw down ratios can be used to reduce polymer alignment in the melt and consequently will reduce shrinkback.

Reducing the DDR down to 4 to 1 is often recommended as a first step to reduce shrinkback. It is understood that there are limits on how low the DDR can be reduced set by excessive die pressures and tooling limitations. It is also important to select tooling that will provide a balanced draw. A high draw balance resulting in the formation of a “tight cone” can sometimes result in higher polymer alignment in the final product. Having the draw balance set at or just below 1.00 is typically recommended when processing PVDF to reduce polymer alignment in the final product.

Running a process “hotter” can also result in a reduction in shrinkback. The reasoning here is that a hotter process will reduce the resins viscosity (easier to flow) and delay the cooling process (longer time in the melt) allowing for a higher level of polymer relaxation in the melt state. Any process change that allows polymer alignment to relax in the melt state prior to freezing will reduce shrinkback. Running the melt temperature or water temperature hotter can sometimes allow more time for relaxation of polymer alignment prior to freezing. Pushing the tank away from the die can also help in this regard as well. Again, there are process safety limitations against having the temperatures set to high as well as jacket concentricity issues related to the distance set between cooling tank and the die.

It is understood that the combination of these tooling/processing changes can result in some reduction in polymer alignment and shrinkback. If process modifications are not sufficient to resolve shrinkback issues, the next step would be to consider alternative PVDF grades having inherently lower shrinkback characteristics.

3. Selection of PVDF Grades for Low Shrinkage Applications

The amount of shrinkback observed in PVDF cable jackets vary tremendously between individual PVDF grades independent of the processing conditions. As a general rule, lower viscosity grades tend to produce lower shrinkback characteristics compared to higher viscosity grades. Shrinkback values greater than 5% have been observed when processing higher viscosity grades. A reduction in shrink back can be obtained simply by changing to a lower viscosity product. Shrinkback values have been observed being cut in half simply by using a low viscosity PVDF grade. Raising the comonomer content reduces crystallinity in the PVDF resin resulting in the production of a softer product amenable to wire and cable applications.

As a cautionary note, there are limitations on “how much” the viscosity can be reduced without having some negative consequence on the physical and mechanical properties of the jacket. Typically, copolymer grades having higher comonomer contents are preferred for wire and cable applications and these grades can be provided at lower viscosity range having good overall properties.

Arkema Inc. offers a wide variety of products that can be used in the wire and cable markets. To explain some of the differences in shrinkage performance, we selected a series of grades that represent a range of products differing in viscosity, comonomer content and distribution. The PVDF materials to be discussed can be found in Table 1.

Table 1: Materials used and their properties.

PVDF ID	HFP Comonomer	Comonomer distribution	η @ 80 s ⁻¹ (Pa.s)	T _m (°C)
K2500-10	High	random	795	127
K2500-20	High	random	1460	114
K2750-01	High	random	2290	140
K3120-10	Moderate	Non-random	650	165
K3120-15	Moderate	Non-random	1230	165
K3120-50	Moderate	Non-random	2390	165

In general, it is understood that lower viscosity PVDF grades exhibit less shrinkback when compared to higher viscosity grades. As an example, K2500-10 (viscosity 795 Pa.s) is known to shrink less than K2500-20 (viscosity 1460 Pa.s). In addition, we discovered that products having a random comonomer distribution would shrink less than those produced having a non-random comonomer distribution. As an example, a random copolymer such as K2500-10 is known to shrink less than a non-random copolymer such as K3120-10 even though both have similar viscosities at 80 s⁻¹. An understanding of the relationship between polymer structure and shrinkback has been gained through numerous studies conducted in the past.

An understanding of the relationship between rheological properties and post shrinkage can be gained by reviewing the complex viscosity of these grades. Dynamic frequency sweep experiments were performed at 190, 210, 230 and 250°C using an ARES-LS strain rheometer. A 25 mm Parallel plate geometry was used at a strain of 5% well within the linear viscoelastic region. The frequency was varied from 100rad/s to 0.01rad/s and the storage and loss moduli as well as the complex viscosity of the samples were generated as a function of frequency. All measurements were conducted under a forced convection of nitrogen gas to minimize degradation. Furthermore, the “Time-Temperature Superposition” principle (TTS) was applied and master curves were generated.

Figure 1 shows the overlay of the viscosity master curves of each PVDF sample at a reference temperature of 230°C. K2750-01 and K3120-50 represent the highest viscosity samples, whereas K2500-10 and K3120-10 represent the lowest viscosity samples. In general, K2500-10 exhibits rheological characteristics that are considered desirable for low shrinkback. An important feature observed in the K2500-10 master curve is the presence of a Newtonian plateau in the low shear region. This characteristic is consistent with our understanding of why this product offers low shrinkage characteristics. Once the melt has been drawn, the melt is in a zero shear state. PVDF materials exhibiting this Newtonian plateau tend to flow better at low shear rates allowing for relaxation of polymer alignment after drawing. The presence of a Newtonian plateau is considered an important feature in PVDF products having low shrinkback characteristics. K3120-10 is a comparable sample also having a low viscosity, but it differs from the K2500-10 by exhibiting a non-Newtonian response at low shear rates. It would be inferred that this

rheological characteristic would delay relaxation of molecular orientation after completion of the drawing operation resulting in higher shrinkback. This has been confirmed through subsequent shrinkback experiments.

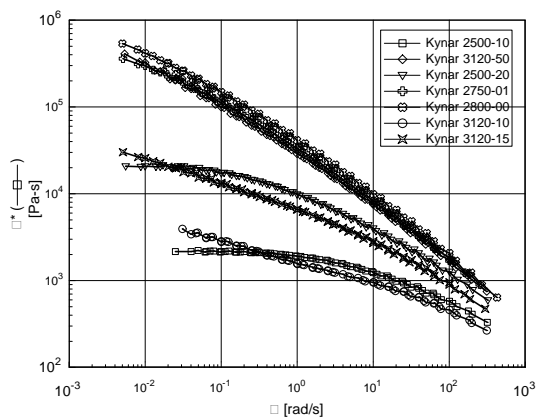


Figure 1: PVDF Master curves – complex viscosity at 230°C

To further understand the relationship between PVDF structure and shrinkback, stress relaxation experiments were performed. It can be reasoned that a polymer having the ability to relieve stresses quickly in the melt state will exhibit lower polymer orientation and consequently lower shrinkback. The stress-relaxation experiments were conducted using the ARES-LS strain rheometer using a 25 mm parallel plate geometry. A step strain of 100 % was applied to PVDF samples and the decay of modulus was recorded as a function of time. Results of these experiments can be seen in Figure 2.

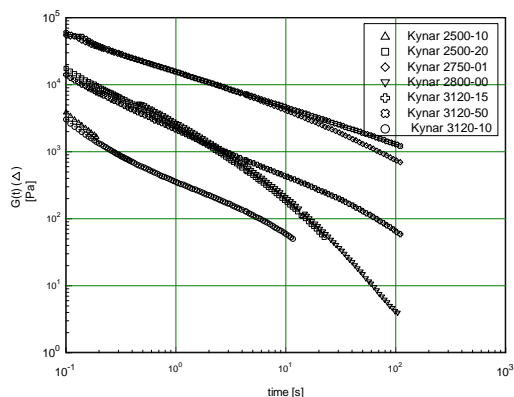


Figure 2: Relaxation modulus of PVDF samples at 230 °C

As expected, the higher viscosity samples such as K2750-01 and K3120-50 show a relatively slow relaxation response whereas the lower viscosity samples such as K2500-10 and K3120-10 exhibit a fast relaxation response. The quick relaxation response for these low viscosity samples should result in less polymer alignment in the final product. For the purposes of this paper, we examined the relaxation times for each PVDF sample to reach the arbitrary value of 100 Pa. These values can be observed in Table 2.

Table 2: Stress Relaxation at 230°C and 100 Pa.

PVDF Sample ID`	Time (s) @ 100 Pa	Viscosity (Pa.s) @ 80 s-1
K2500-10	0.65	795
K3120-10	2.0	650
K2500-20	6.8	1460
K3120-15	10.0	1230
K2750-01	220	2290
K3120-50	400	2390

As can be seen in Table 2, the relaxation response for the K2500-10 is considerably faster than any of the other products tested. A significant amount of this behavior can be attributed to the structure of this product. When comparing K2500-10 to K3120-10, it is noted that the relaxation response for the K2500-10 (random copolymer distribution) is significantly faster than for the K3120-10 (non-random copolymer distribution). The faster relaxation response was predicted from the master curve (Figure 1.), which showed the rheological differences of these two products in the low shear range.

When interpreting the data, it is beneficial to have an understanding of the cooling environment typical for PVDF processing. In a standard jacketing operation producing a 0.020 inch jacket and run at 300 feet per minute with a 6 inch gap between the cooling tank and the die, it was estimated that the time from the end of drawing and before entering the tank will be 0.10 seconds, and the actual time to solidify the jacket will be approximately 0.42 seconds for a total cooling time of 0.52 seconds. Based on this approximation, the K2500-10 will have sufficient time to relax after the drawing operation. Conversely, the higher viscosity samples as well as the non-random samples will not have relaxed in this time period and it would be assumed that the majority of the elastic stresses will be frozen into the resultant jacket.

With the knowledge of the rheological characteristics necessary to achieve low shrinkage properties, and analytical methods developed to screen new materials, efforts to further improve low shrinkage characteristics in PVDF have been initiated. PVDF structures already identified as having low shrinkage characteristics were modified for possible further improvement.

Two existing commercial grades of PVDF identified as PVDF 1A and PVDF 2A were characterized for shrinkback by conducting a series of shrinkback experiments on cables jacketed with these products. Cable jackets were applied in-house using a small lab extrusion line consisting of a 1-inch Killion extruder outfitted with a BH-30 cross head and all the necessary down stream equipment. Conditions such as barrel temperature, water temperature, line speed, tank distance etc. were all standardized to eliminate these as variables in the experiment. Cables were cut in 10 foot lengths and the jackets were removed by slitting the length of the cable. Shrink back experiments were conducted by measuring the jacket length before and after a thermal exposure of 121°C for 1 hour. A 24 hour recovery period was allowed before taking the final measurement.

Shrinkback experiments were repeated using similar PVDF products having some modifications to the structure with the goal of further reducing shrinkback characteristics. These samples are

identified as PVDF 1B and PVDF 2B. A summary of the results from shrink back experiments can be found in Table 3.

Table 3. Shrinkback experiments on PVDF cables

Material	% Shrinkback
PVDF 1A (existing commercial grade)	2.97
PVDF 1B (improved PVDF 1)	-0.28
PVDF 2A (existing commercial grade)	1.22
PVDF 2B (improved PVDF 2)	0.29

The existing commercial grades chosen had characteristics that were already considered relatively low shrinkage products for cable applications. The adjustments in the rheological characteristics had the desired effects of further reducing the amount of shrinkback observed for this product. It was shown that these adjustments had no negative impact on the characteristics of the cable. The negative value listed for PVDF 1B is an indication that the cable was slightly larger after the thermal exposure. It is believed that this is an indication of zero shrinkage and the negative value is within the accuracy range of the experiment.

4. Conclusions

Post shrinkage is understood as a problem in the fiber optic industry because of its effect on cable performance due to excess fiber length. It is understood that the problem with shrinkage is primarily due to polymer orientation being frozen in to the PVDF post processing. The wire and cable process requires the product to be drawn in the melt state resulting in significant polymer alignment. Due to the high speed nature of the cable jacketing, and the relatively quick cooling inherent to the process, much of the stresses produced are frozen into the final product. Post shrinkage or shrinkback is simply caused by the relaxation of these stresses in the solid state. To reduce shrinkback, tooling and processing conditions can be optimized to reduce polymer alignment and to increase the time available for subsequent relaxation. Changes in the processing conditions that allow the PVDF to remain in the melt state after drawing will have an effect on the total amount of polymer alignment remaining after solidification.

We learned that the rheological characteristics of the PVDF have a significant effect on post shrinkage. PVDF structures that allow for faster relaxation of polymer alignment will exhibit lower shrinkback. Lowering the viscosity was shown to be one means of reducing shrinkback. Modifications of the polymer structure to provide a more Newtonian response in the low shear region is another. Arkema has used this understanding to develop new low shrinkage grades for the fiber optic market.

5. Acknowledgments

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6. References

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Authors



James (Jim) Henry is a Senior Research Engineer at Arkema Inc. located in King of Prussia, PA. James received a Bachelors Degree in Chemical Engineering in 1986 from the University of Lowell, and his Masters Degree in Plastics Engineering in 2003 from the University of Massachusetts. Jim joined Arkema Inc. (Formerly Atofina Chemicals) in January 2001, and currently focuses his efforts with developing and researching PVDF products in the W&C and the Chemical Processing markets.



Dr. Nafaa Mekhilef is a Senior Research Scientist with Arkema, Inc in King of Prussia, PA. He has expertise in polymer structure and rheology and its correlation with melt processing. His research interests are in the area of rheological properties of complex fluids, polymer blends and non-random systems.