RESINATE

No. 4, JULY 2017

RESINATE

Your quarterly newsletter to keep you informed about trusted products, smart solutions, and valuable updates.

A NEW LOOK AT PTFE AND THIN-WALLED CATHETER LINERS

KEVIN J. BIGHAM, PhD.

ZEUS®

INTRODUCTION TO PTFE

PTFE, or polytetrafluoroethylene, is a highly popular and abundantly useful fluoropolymer. PTFE has been with us since the 1930s when it was created by accident by technicians working for DuPont. PTFE is unique as a fluoropolymer in that it is fully fluorinated containing only fluorine and carbon atoms (**Fig. 1**). This structure gives PTFE many unique and desirable properties. In fact, according to recent estimates, the global PTFE market is expected to reach USD 6.44 billion by the year 2020 showing a combined annual growth rate of 8.1 % [1]. This translates into an estimated global consumption of PTFE of 524.1 kilotons within the next three years [1]! We know PTFE primarily as Teflon® and its familiarity as a non-stick coating for cookware, but as this market overview shows, PTFE has become a mainstay in vast areas of our modern world.

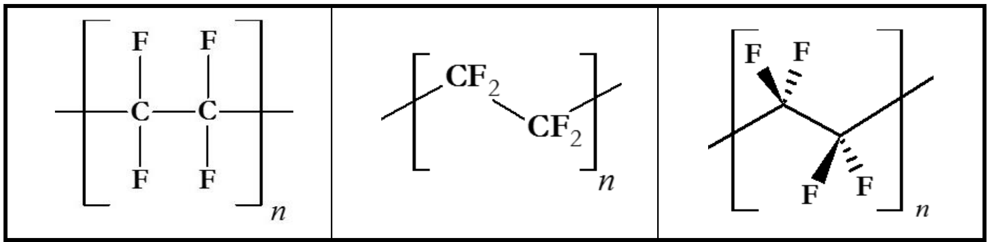


Figure 1: Classical depictions of PTFE monomers shown in Lewis structure (*left*), bond-line drawing (*center*), and stereo representations (*right*).

STRUCTURE OF PTFE

PTFE is a homopolymer of tetrafluoroethylene (TFE) and is made by combining tetrafluoroethylene monomers via a radical reaction (**Fig. 2**). TFE polymerization is catalyzed by peroxide included in the reaction, and the resulting reaction is self-sustaining until quenched or reactants are exhausted. The result of this reaction is long-chain (high molecular weight) molecules with significant strength. PTFE chain length is widely controllable and thus can be manipulated to suit specific applications. Unlike most saturated carbons compounds, however, PTFE polymer chains are generally not flexible; they form rigid rod-like molecules with unique chemical character.

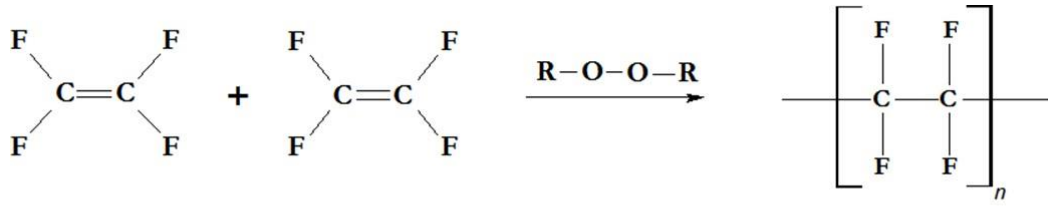


Figure 2: General reaction scheme for the synthesis of PTFE.

PTFE's distinctive properties stem from its multiple C–F bonds. Fluorine has the highest electronegativity – its attraction for electrons including those involved in bonding – of any element on the periodic table [2, 3]. Carbon possesses moderate electronegativity compared to fluorine, thus the C–F bond is highly polarized towards fluorine. In addition to covalent sharing of electrons between carbon and fluorine, there are significant electrostatic attractive forces drawing the partially positive carbon ($C^{\delta+}$) towards the partially negative fluorine ($F^{\delta-}$). Thus, the covalent nature of the C–F bond coupled with its partial electrostatic character result in a C–F bond that is very short, and this effect is compounded with multiple C–F bonds in PTFE through multiple dipole interactions. C–F bond length in PTFE is typically on the order of 1.32 Å and for a C–F bond length in general is 1.35 Å [4]. This length is shorter than other carbon-halogen bonds and shorter than C–O and C–N bonds. (Only the C–Si bond is shorter than a C–F bond). The result is a close packing of PTFE along the C–C backbone, but in an unexpected manner.

PTFE is a close-packed long-chain polymer. PTFE, however, does not adopt the typical zig-zag pattern observed for most saturated carbon chains but is instead helical (**Fig. 3A**). Normally, larger substituents on adjacent carbons along a carbon chain backbone would position themselves in an *anti* conformation (**Fig. 4A**). However, because of the large size of fluorine atoms and their high degree of electron density stemming from their electronegativity, the fluorine atoms on adjacent carbons of PTFE cannot form a true staggered and *anti* conformation. Instead, the fluorine atoms arrange themselves along the carbon backbone in a helical conformation with dihedral angles along C–C atoms of slightly less than the 60° of a staggered *anti* conformation (**Fig. 3B** and **4**).

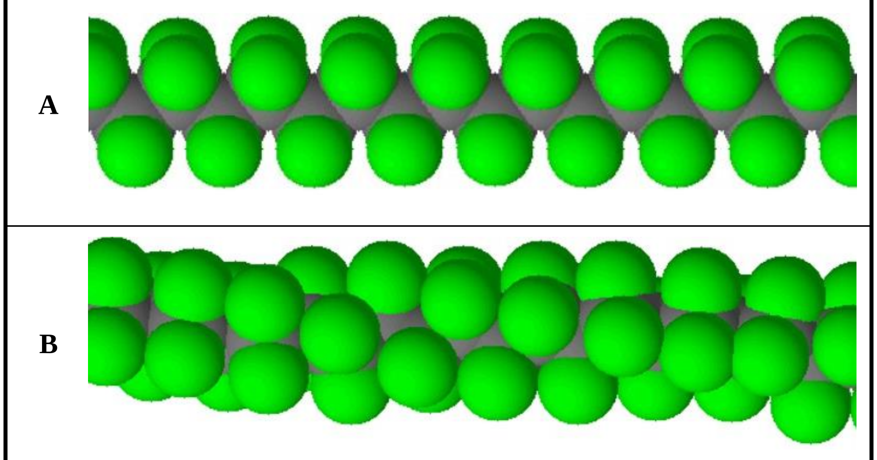
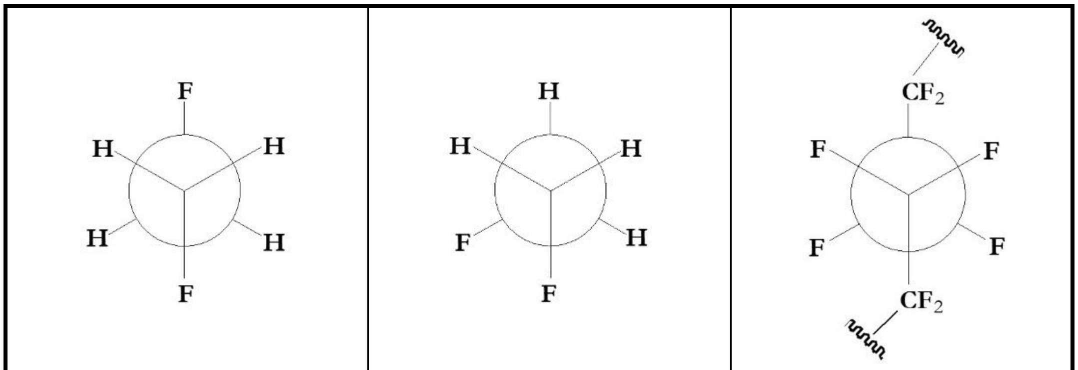


Figure 3: (A) Typical zig-zag conformation of a saturated hydrocarbon chain. (B) PTFE helical geometry with fluorine atoms surrounding the carbon chain backbone.

This unusual phenomenon of PTFE is due not to the *gauche* effect suggested in small fluorinated alkanes but to hyperconjugation and interaction of the C–C bonding and C–F anti-bonding orbitals ($\sigma CC \rightarrow \sigma^* CF$) of PTFE (**Fig. 5**) [5]. The decrease in energy due to hyperconjugation more than outweighs the energy penalty resulting from the smaller dihedral angle along adjacent C–C atoms. These energy benefits become more pronounced with each additional –CF_2–. The result is an even more closely packed helical PTFE with a high degree of stability. This preferred helical conformation of PTFE over the zig-zag conformation is so stable, in fact, that it has also been observed in perchlorinated alkanes [5]. (It should be noted that PTFE exists in at least two other phases or transitional conformations of varying degrees of helicity, depending on temperature and pressure, of which Phase II dominates at approximate room temperature and below [6-8]. These phases shall not be discussed here, however).



staggered *anti* conformation

gauche conformation

staggered conformation (PTFE)

Figure 4: Newman projections: Geometry comparison of small fluorinated alkanes and PTFE. The staggered *anti* conformation of 1,2-difluoroethane, $C_2H_4F_2$ (*left*), the *gauche* conformation of 1,2-difluoroethane (*center*), and the zig-zag staggered conformation of PTFE (*right*).

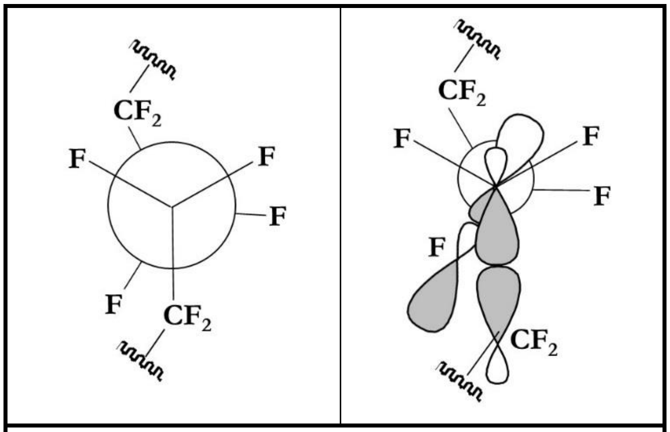


Figure 5: PTFE helical geometry illustrations: The exaggerated (*quasi*-) *gauche* conformation of PTFE (*left*), and same showing σCC→σ*CF orbital interaction and hyperconjugation (*right*).

FEATURES AND PROPERTIES OF PTFE

PTFE's close-packed nature together with its fully bonded carbon chain give this polymer a multitude of preferable properties that have placed it in such demand today. With its high electron density, fluorine's three lone pairs of electrons balance the overall dipole moment irrespective of its C–F bond. This means that the fluorine atoms of PTFE are non-polarizable. The fluorine atoms of PTFE also have a complete valence shell octet of electrons. These two aspects render fluorines of PTFE poor electron donors and poor hydrogen bond acceptors. The result is an unreactive sheath of fluorine surrounding the C–C backbone of PTFE giving PTFE extremely good chemical resistance. (PTFE can still be affected by specially prepared conditions involving alkali metals or halogenated compounds, however).

The unreactive fluorine sheath of PTFE also has other important implications. PTFE's outer compact fluorine "capsule," with its high electron density, mutually repulses other PTFE chains. As a consequence, PTFE surfaces have an extremely low coefficient of friction, typically reported in the range of 0.02 – 0.08. The unreactive nature of PTFE towards even small molecules such as water or other PTFE chains means that PTFE adheres to almost nothing. These features translate into extremely good lubricity for specialized applications.

PTFE is also a rigid molecule. Unlike less halogen-saturated carbon chain polymers or simple hydrocarbon chains such as polyethylene, PTFE does not allow free rotation around the C–C backbone single bonds. The electron density and the space required for the electrons of the fluorine atoms results in steric repulsion through vicinal positions but also through the 1,3-positions. Such repulsions make the rotational energy barrier about the C–C single bonds highly unfavorable, hyperconjugation notwithstanding. The result is a conformationally inflexible PTFE polymer chain.

PTFE PRODUCTS AND CATHETER COMPONENTRY

PTFE can be fabricated in a variety of products. PTFE's mechanical and chemical features allow these products to be used in a wide range of applications. PTFE can be formed into molded parts; used as flexible pipe joints, valve bodies, electrical insulators, bearings, gears; and extruded as tubing (**Fig. 6**). PTFE can be machined into precision parts with very fine tolerances and can be made into thin sheets or film and even heat shrink. PTFE's tight-bonded nature manifests itself in excellent wear and abrasion resistance with supreme lubricity.

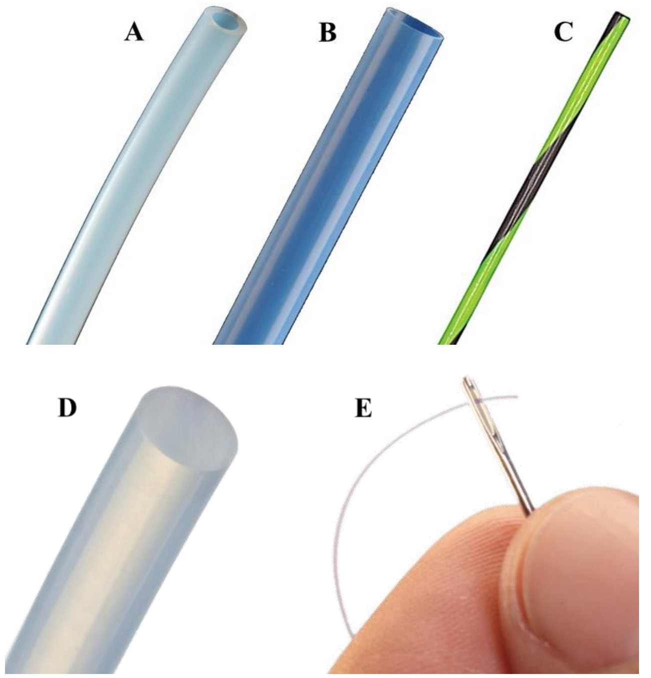


Figure 6: Example PTFE extruded products: (A) unpigmented and (B) pigment tubing, (C) PTFE heat shrink with spiral pigmenting, (D) PTFE monofilament (close-up view), and (E) Zeus PTFE Sub-Lite-Wall® tubing. (*Images not to scale*).

With such properties as chemical resistance and lubricity, it is not surprising that PTFE found its way into medical applications where these features are especially desirable. PTFE has a long history of safe and successful use in the medical industry dating back before the 1970s [9]. PTFE can be extruded as tubing with extremely thin walls making it ideal for vascular catheter componentry where small size and uniform diameters are paramount. PTFE can be used, for example, for the inner wall (base liner) of guiding catheters to provide an exceedingly smooth inner surface. The smooth PTFE inside diameter (ID) of these catheters reduces friction against various catheter technologies such as stents, balloons, or atherectomy devices as they are pushed through the tight confines of the catheter lumen. If the catheter ID is not of sufficient lubricity, devices such as stents can collapse in an accordion-like manner as they are being pushed through the catheter lumen. The effect of increased lubricity of the catheter ID is a reduced deployment force of catheter devices as they are passed through the lumen increasing the likelihood of a successful procedure.

DIP-COATING VS. FREE EXTRUSION FOR CATHETER BASE LINERS

A competing technology for achieving thin polymer walls over a component is dip coating. This process is performed to impart some surface attribute or quality to the coated part such as lubricity or increased rigidness. In the instance described here, dip coating can be performed onto a mandrel as part of the catheter construction process. Then, once the coating has cured, the additional components of the catheter, including braiding, nylon jacketing, and a jacket re-flow process step are built upon the cured dip-coated mandrel (**Fig. 7**). Once the catheter construction is complete, the mandrel is then removed from the newly built catheter leaving behind the dip-coated layer which becomes the innermost lumen wall.

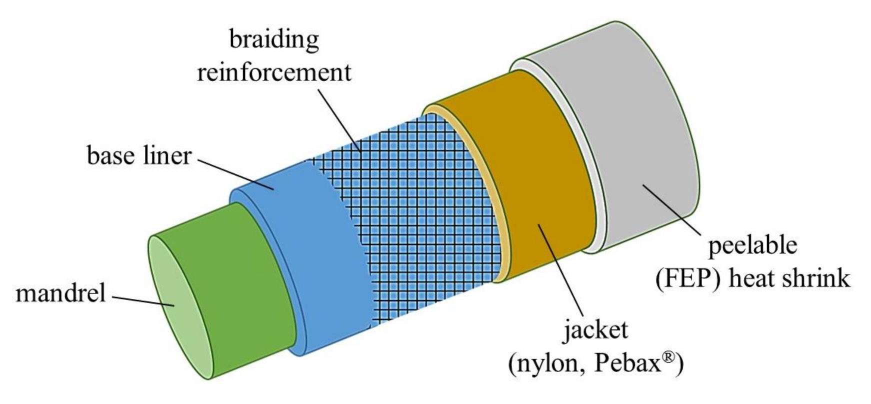


Figure 7: Catheter construction: basic catheter components: mandrel, base liner, braiding reinforcement, jacket (nylon or Pebax® typical), and peelable (FEP) heat shrink.

While appearing to be a simple process at the outset, dip-coating has some limitations that prevent it from being universally used for catheter construction. Dip coating can experience unevenness resembling the surface of orange peel. Dip-coated surfaces can sometimes have the appearance of many cross-sectional lines known as chatter resulting from vibrations during the coating process. Dip-coated surfaces can also have depressions, craters, or even holes in the cured layers caused by contaminants – including moisture – during the coating process. Surface defects of the catheter ID represent a serious impediment to catheter use. While these defects can be addressed in various ways, greater precision of the dip-coating process will usually entail greater time and cost.

Lastly, also partly due to the defects described above, dip-coated mandrels for catheter ID lumen wall can experience poor adhesion. These deficiencies can be in the form of poor adhesion of the dip-coated layer (liner) to the mandrel itself or poor adhesion of the liner to the jacket laid down over the braiding. Imperfect adhesion can result in delamination defects, the most serious defect for catheter liners. Such failure can affect the fundamental aspects of the catheter such as torsional transmittance, pushability, or deflectability. The end result of such a defect is likely a failure of the catheter itself. While rare in occurrence, delamination defects present a serious added risk regarding the dip-coating process.

ULTRA-SMALL (MICRO) CATHETERS AND THEIR APPLICATIONS

Driving the pursuit of thin-walled extrusions and the dip-coating process for catheter construction is the demand for ever-smaller sized devices. Falling under the general description as micro-catheters, these devices are needed to navigate very small vasculatures for minimally invasive surgical procedures (MISPs). These procedures may be investigation, diagnostic, mapping, or interventional in nature. Catheter design is balanced between construction and functionality. Fundamental targets focus on catheter pushability, trackability, flexibility, and torqueability (torsional force or transmittance). Depending on the tortuosity of vasculature being explored, catheter outside diameter (OD) as well as ID play a role in selecting an appropriate design and device for the application. Catheter ID wall thickness, thus, is a trade-off of the desired fundamental catheter functional attributes and application environment.

ZEUS SUB-LITE-WALL® STREAMLINER™ CATHETER LINER

Advancing micro-catheter designs to meet the needs of cardio-, peripheral, and neurovascular markets is a daunting task. The demand for smaller and more functional devices is continuous. In light of these needs, Zeus Industrial Products, Inc., is producing their new Sub-Lite-Wall® StreamLiner™ series of thin-walled catheter liners. Zeus Sub-Lite-Wall® tubing, already reaching wall thickness to 0.005″ (0.127 mm) and below, now has been made even smaller with StreamLiner™ series of thin-walled catheter liner extrusions. These specialty extrusions are made from PTFE and build upon the long-standing success of Sub-Lite-Wall® products from Zeus. These thin-walled extrusions were initially created to give medical device engineers and manufacturers greater access to the body's tortuous pathways. Now with the state of this market driving access to smaller and smaller vasculatures, Sub-Lite-Wall® StreamLiner™ series of PTFE extrusions is poised to become the market standard.

The first offering from Zeus in the StreamLiner™ series, StreamLiner™ XT, improves upon their already best-in-class thin-walled catheter liner. Featuring Zeus' LoPro™ proprietary technology, StreamLiner™ XT possesses a maximum wall thickness of 0.00075″ (0.01905 mm) and can be produced with IDs as low as 0.013″ (0.330 mm) (**Fig. 8**). These super-small walled catheter liners allow for smaller finished device outside diameters (ODs) while also creating increased catheter lumen potential. PTFE's high lubricity is of particular advantage, too, because it results in improved (decreased) deployment force within the catheter lumen for the technology (camera, fiber optic, etc.) that is being pushed through it.

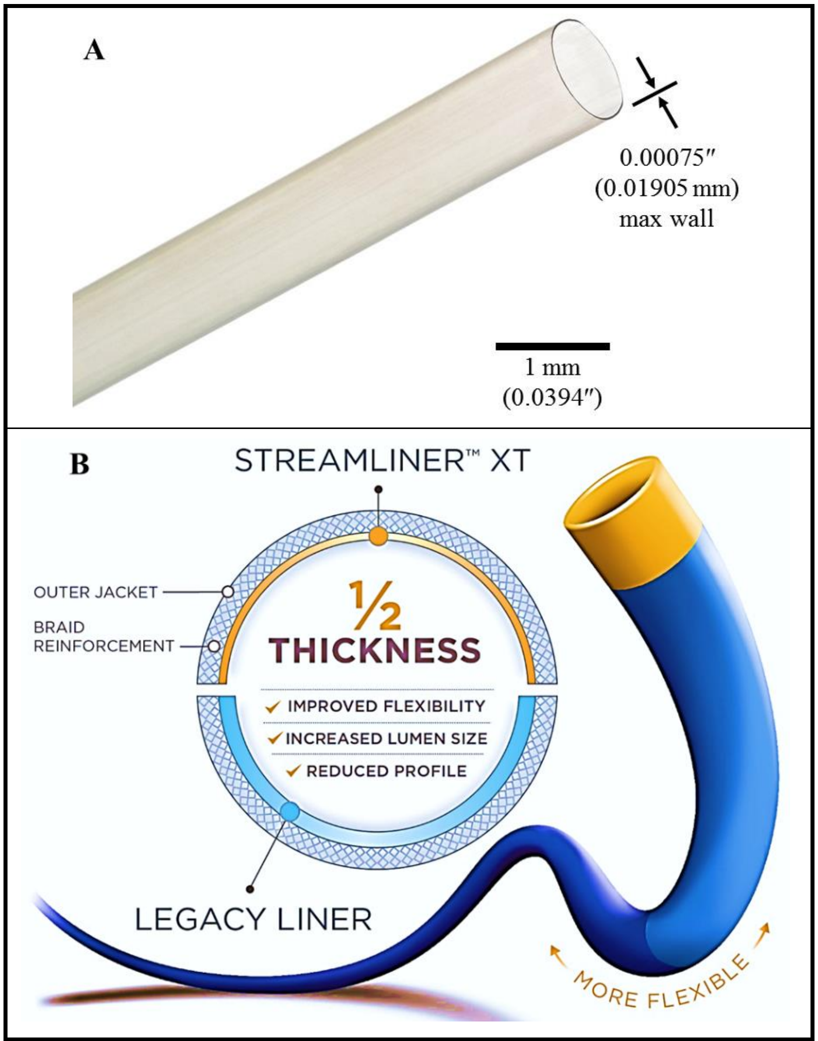


Figure 8: Sub-Lite-Wall® StreamLiner™ XT: (A) StreamLiner™ XT extruded tubing, and (B) schematic, graphic illustration, and feature description of StreamLiner™ XT.

As a free extrusion, StreamLiner™ XT has several advantages over dip-coating. These PTFE liners are stronger and tougher than conventional liners. StreamLiner™ XT does not experience the depressions, craters, or holes to which dip-coated liners are susceptible. The uniformity of StreamLiner™ XT thus contributes to its super-smooth lumen ID surface finish. StreamLiner™ series of liners are also not prone to delamination as can happen with dip coated liners. Together, these improvements enable the Sub-Lite-Wall® StreamLiner™ series to reduce risk to patients while providing a high performance and effective alternative to dip-coating for successful patient outcomes.

SUMMARY

PTFE is a synthetic fluoropolymer first discovered in the 1930s which has grown into a world-wide industry. PTFE's fully fluorinated nature contributes to this polymer's unique helical structure producing a variety of beneficial properties. With such favorable properties as low coefficient of friction and superior chemical resistance, PTFE made its way into the medical sector and has a long-established history of successful use there. Improving upon PTFE extrusion technology, Zeus Industrial Products, Inc., has produced an ultra-thin-walled PTFE catheter liner introduced as their Sub-Lite-Wall® StreamLiner™ series. The first offering from this series and featuring Zeus' proprietary LoPro™ technology, StreamLiner™ XT, improves upon Zeus' already best-in-class wall thickness to produce a liner with ≤ 0.00075″ (0.01905 mm) wall thickness. As a free extrusion, the StreamLiner™ series eliminates many of the risks of a competing technology, dip-coating, such as uneven lumen wall surface and delamination. These liners make for a sturdier or more robust finished device while retaining sufficient functional properties such as torquability pushability, and flexibility. The super lubricious catheter lumen ID greatly improves deployment force through the catheter for successful MISPs. Sub-Lite-Wall® StreamLiner™ XT allows greater access to small vessels including peripheral and neurovasculatures and represents a new tool for medical device engineers and clinicians to improve patient outcomes.

ABOUT ZEUS

Zeus is the world’s leader in polymer extrusion technologies. For over 50 years, Zeus has been serving the medical, aerospace, energy exploration, automotive, and fiber optics industries. Headquartered in Orangeburg, South Carolina, Zeus employs approximately 1,250 people worldwide and operates multiple facilities in North America and internationally. You can find us at www.zeusinc.com.

CONTACT US

More information regarding the material discussed here is available by contacting a Zeus technical account manager. They can be reached in the US toll-free at **1-800-526-3842** or internationally at **+1-803-268-9500**. You can also email us at editor@zeusinc.com.

Zeus Industrial Products, Inc.
3737 Industrial Blvd.
Orangeburg, SC 29118
USA

REFERENCES:

1. **Polytetrafluoroethylene (PTFE) Market Worth $6,440.0 Million By 2020**. In. Online: Grand View Research; 2015.
2. Pauling L: **The chemical bond: a brief introduction to modern structural chemistry**: Cornell University Press; 1967.
3. Pauling L: **The Nature of the Chemical Bond and the Structure of Molecules and Crystals: An Introduction to Modern Structural Chemistry**: Cornell University Press; 1960.
4. O'Hagan D: **Understanding organofluorine chemistry. An introduction to the C-F bond**. *Chemical Society Reviews* 2008, **37**(2):308-319.
5. Cormanich RA, O'Hagan D, Bühl M: **Hyperconjugation is the Source of Helicity in Perfluorinated n-Alkanes**. *Angewandte Chemie International Edition* 2017:n/a-n/a.
6. Tanaka H, Takemura T: **Studies on the High-Pressure Phases of Polyethylene and Poly(tetrafluoroethylene) by Raman Spectroscopy**. *Polym J* 1980, **12**(6):355-361.
7. Clark ES: **The molecular conformations of polytetrafluoroethylene: forms II and IV**. *Polymer* 1999, **40**(16):4659-4665.
8. Wang C, Duscher G, Paddison SJ: **Electron energy loss spectroscopy of polytetrafluoroethylene: experiment and first principles calculations**. *Microscopy* 2014, **63**(1):73-83.
9. Laustriat S, Geiss S, Becmeur F, Bientz J, Marcellin L, Sauvage P: **Medical history of Teflon**. *Eur Urol* 1990, **17**(4):301-303.