

“Generational Advancements in Fluoropolymer Lined Piping Systems”



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ABSTRACT

Polytetrafluoroethylene, or PTFE, is a widely used plastic suitable in countless applications. Its unique properties, from chemical inertness, low thermal and electrical conductivity, high temperature resistance and mechanical strength, make it an ideal solution to many application challenges. In particular, these properties are widely exploited in chemical process applications. When molded and installed in a metallic housing, the resulting composite system offers users a truly unique option in the industry, a piping system with the chemical inertness of PTFE, and the strength of the steel housing which process engineers had come to depend on since the early days of the industrial revolution.

Following World War II, a revolution took place within the chemical processing industry as new fluoropolymer-based piping designs were qualified and used with great success. At the same time, competition increased among plastic-lined piping suppliers worldwide, and those suppliers sought technical differentiation. In an industry where technical differences were sometimes quite subtle, a great deal of anecdotal information has been used in the promotion process. In some cases, inferences were drawn from data which were not strictly logical or fact-based. The net result has been devolution of the quality of the technical argument for individual product offerings. This paper is designed to inject facts back into discussions and thus empower end-users, specifiers and sellers, as to the salient points to know and inquire about when selecting plastic-lined piping systems.

Recent developments in PTFE processing have achieved significant improvements in permeation control and understanding of this property. Collectively, the improvements have come to be considered a generational step forward for the plastic-lined piping industry, and thus are termed "Next Generation" plastic-lined pipe and fittings. Although specific methodologies are proprietary, a primary intent of this paper is to highlight performance differences between the Next Generation of plastic-lined pipe and fitting and all previous offerings in the industry.

This paper seeks to provide practical insight on the phenomenon of permeation in plastic lined piping. This is followed by technical overview of differentiating factors of three common PTFE pipe liner manufacturing techniques. Finally, the results of practical experimentation conducted by the authors and others will be presented and used to support the claims of this paper.

OVERVIEW

Polytetrafluoroethylene, or PTFE, is a widely used plastic suitable for countless applications. Its unique properties, from chemical inertness, low thermal and electrical conductivity, high temperature resistance and mechanical strength, make it an ideal solution to many application challenges. PTFE was invented by Roy J. Plunkett, researcher for El DuPont DeNemours, just before World War II, (reference U.S. patent number 2,230,654). At this time, the industry was just beginning to understand the uses for this new material. One early important use of PTFE was as a liner for flexible hoses in aggressive chemical services; a natural evolution of this concept was to use the new plastic as a liner for the more permanent installations in chemical plants – the process piping. This composite system offered users a truly unique option in the industry, a piping system with the chemical inertness of PTFE, and the strength of the steel housing which process engineers had come to depend on since the early days of the industrial revolution.

In parallel with these developments, innovation in the plastic industry itself was burgeoning. DuPont and other plastic manufacturers realized that many of the unique properties of PTFE were directly attributable to the strength of the chemical bond of the carbon-fluorine chain in the backbone of the PTFE molecule. This same chemical bond also introduced processing complexity as the material is so viscous at melt temperatures that standard manufacturing methods for plastics, such as extrusion or injection molding, are simply not feasible for PTFE. Rather, special manufacturing techniques are required, which became a barrier to acceptance as few plastics processors were willing to invest in the specialized equipment required to produce PTFE. This proved to be the motivation for development of other fluorine containing plastics, all grouped into the overarching category of fluoropolymers. Modification to the basic carbon-fluorine backbone, primarily in the form of side chains, introduced new properties that enhanced processability and, in most cases, altered cost and performance.

Within the chemical processing industry, a revolution took place as new fluoropolymer-based piping designs were qualified and used with great success. At the same time, competition increased among plastic-lined piping suppliers worldwide, and those suppliers sought technical differentiation. In an industry where technical differences were sometimes quite subtle, a great deal of anecdotal information was used in selling. In some cases, inferences were drawn from data which were not strictly logical or fact-based. The net result has been devolution of the quality of the technical argument for individual product offerings. This paper is designed to inject facts back into the discussion and thus empower end-users, specifiers and sellers, as to the salient points to know and inquire about when selecting plastic-lined piping systems.

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In particular, the phenomenon of permeation has been widely expounded upon, however, not always factually. It is, at bottom, a simple three stage physical process involving the absorption of a fluid into its container wall, diffusion through that wall, and escape, or evaporation on the exterior of that container wall. In the case of plastic-lined piping, that container is intimately and completely surrounded by the metallic housing, although infinitesimal interfacial gaps do exist. The housing may or may not be vented to atmosphere. The permeation phenomenon is of deep interest to plastic-lined piping users, as the plastic wall, regardless of the exact type of plastic or piped media, is known to permeate at rates much higher than alternate piping systems, such as the solid metals. This is relevant to these users only in light of the subsequent potential for harm done by the permeating chemical species.

The harm can take several forms:

1. Fugitive emissions, or unintended escape of process media, which are potentially dangerous and a target of increasingly strict regulation.
2. Damage to the outer shell, reducing the sought after strength of the reinforcing housing, and thus also creating potentially unsafe conditions.
3. Deformation of the liner - housing interface through the buildup of corrosion byproducts. This can degrade the liner's vacuum resistance and, in extreme cases, seriously impinge flow of fluid through the pipe.

Fugitive emissions generally occur throughout the length of time a lined piping component is in service, beginning after a lag known as "break-through time" and increasing gradually until a steady state is reached; this will continue as long as the media and its motive force are present in the component. The motive force derives from the media vapor pressure, itself temperature-dependent.

The second and third items noted above also begin at the break-through time, but are generally only detectable via inspection or when a significant problem results, such as catastrophic shell failure or when an unacceptable pressure drop is noted. These detections generally signal the end of the product's useful life. All these effects have been perceived in actual applications and are also the subjects of claims of varying veracity made by producers of plastic-lined piping products. The following section will provide information as to the factors that impact permeation.

Key Factors Affecting Permeability

Fundamental understanding of the permeation phenomenon is not the aim of this present document. Readers interested in an academic treatment are encouraged to study the appropriate reference materials noted in the appendices. This paper will provide a practical primer on permeation, with a particular aim at plastic-lined piping installations. The results of practical experimentation conducted by the authors and others will be used to support the claims of this paper. At a high level, most of the factors affecting permeation are relatively simple and intuitive; others require a brief exploration of some more subtle aspects of the physical process at work in permeating systems.

Vapor Pressure

Often, permeation is considered strictly in terms of outward effects and is equated with leaking. This however, is not entirely accurate. Where the distinction applies is important because, unlike leakage, for liquids, the phenomenon is essentially independent of applied system pressure; instead vapor pressure in liquid piping systems is important. If there is an unhindered region outside the lining, vapor pressure is known to be directly related to permeation rate. If instead there is some hindrance in this outer region – e.g. an unvented pipe wall - as permeation proceeds, vapor will build up in the hindered region; the driving force for further permeation is then the difference in vapor pressure on either side of the lining, and is thus reduced compared with the initial stages. Thus, when considering the severity of service and projecting rate of permeation, the value of importance when a liquid is present is the pressure of its vapor present in systems which are less than hydraulically filled.

In contrast, if the fluid is gaseous, vapor pressure **is** actual pressure; so that for a gas, permeation may be seen as a miniscule form of leakage. It should be noted that some aqueous fluid mixtures, when at high temperatures, may involve gas dissolved in water; in this case, the driver for any water permeating will be its partial vapor pressure, whereas the gas will be driven by its 'partial actual pressure'.

Liner Wall Thickness

Liner wall thickness is inversely related to permeation rate; essentially, a doubling of wall thickness will, all other things being equal, halve the permeation rate. To fully understand this fact, one must first appreciate the concept of a concentration gradient that is present in permeating systems with unrestricted escape on the exterior surface. On the wetted side of a permeating system, the wall is fully saturated when at steady state. Just beneath the skin, the diffusion activity ensures that the wall is less than fully saturated. When steady-state conditions have been reached, the concentration continues to reduce linearly until, on the exterior, any molecules of permeant are removed by evaporation and the concentration is near zero. It is intuitive to think of the wall as eventually achieving full saturation but, in practice, this virtually never happens in vented PTFE lined piping systems. A good analogy for the situation with unrestricted exterior escape is the temperature gradient through an insulated building wall; the effect of increasing insulation thickness is to thermal transfer exactly as wall thickness is to permeation rate.

In a pipe situation, escape is not unrestricted. This means that a vapor pressure of the permeant begins to build up in non-touching regions between lining and pipe wall, and the 'line' of permeant molecules still within the lining waiting to escape at the exterior become increasingly held up. Thus the concentration slowly increases within the lining and the drive for permeation reducing accordingly. Eventually, if the non-touching regions are not joined and/or not vented to atmosphere, theoretically a fully saturated situation could arise. It is likely in practice that some escape always happens, but nevertheless, in time a concentration increase will happen within the lining.

Permeating Molecule Size

Permeating molecule size seems to be an obvious factor in permeation rate; the larger the molecule of the permeating species, the lower the permeation rate. For liquids, permeation occurs because most are soluble to a lesser or greater extent in the amorphous regions of plastics. On a molecular level, what this means is that after the adsorption stage the liquid migrates by diffusion through the plastic by jumping into intermolecular voids that exist in all polymers, formed transiently by kinetic-energy-driven motion. Therefore, it is important to consider not just the molecule size of the interior liquid, but also the molecule size of the permeant. In addition, some permeant molecules are chemically attracted to the plastic, e.g., by hydrogen bonding, which can cause swelling in some instances. Genuine chemical attack is also possible, but unlikely to be met in practice providing well-established plastics have been selected for the service. The bottom line is that knowing the molecule size of the process media may or may not be an indicator as to the ultimate permeation rate.

Solubility Coefficient

Fluids are soluble in polymeric materials. The amount (mass) of liquid which can be absorbed by a given volume of polymer is given by the solubility coefficient multiplied by vapor pressure (atmospheres or bars), and the volume of gas likewise is given by the solubility coefficient multiplied by actual pressure; the units for solubility coefficient are different in the two cases to allow for this subtly-different definition. In simple terms, it is a measure of the affinity a permeant molecule has for the plastic container wall material. Increasing affinity or wettability correlates directly to permeation rate.

Crystallinity

On a molecular level, most plastics exhibit randomly located areas of ordered crystalline structure scattered throughout amorphous arrangements of molecules. These crystalline arrangements are effectively small, void-free zones which, among other effects, inhibit permeant progress. The permeating molecules are thus forced to migrate along an alternate route. This has the net effect of slowing the overall permeation rate. There are two reasons for this effect. The commonly referred to point is that individual molecules are prevailed upon to adopt a more tortuous route. Equally or perhaps more significant is the traffic jam effect. As mentioned above, permeation is a physical process and permeants migrate through a container wall by making a series of jumps

from void to void when they are near enough and large enough to accept the permeant. When a crystallite is encountered, not only must the permeating molecule adopt an alternate route, but it is statistically more likely that nearby voids are already occupied and thus unavailable to accept new passengers.

This particular factor of crystallinity is relevant because, as it happens, it is one of the more cost effective and practical tools available to lined piping designers that helps to achieve significant gains in permeation rates. Additionally, processors of fluoropolymers have collectively developed internal standards and controls to improve the crystalline nature of their products. Recent developments in the market have achieved significant improvements in, and understanding of this, property. Collectively, the improvements have come to be considered a generational step forward for the plastic-lined piping industry, and thus are termed "Next Generation" plastic-lined pipe and fittings. Although specific methodologies are proprietary, a primary intent of this paper is to highlight performance differences between the Next Generation of plastic-lined pipe and fitting and all previous offerings in the industry.

Temperature

As mentioned previously, the inter-molecular voids present in all plastics are the vehicle through which permeants travel; their molecules jump from void to void as they become available. The voids move (and thus become available) as a result of the kinetic energy of the plastic molecules. The temperature of a system is, of course, a direct measurement of the molecular kinetic energy. Thus, physics dictates that higher temperature means faster moving voids which, in turn, provides increasing statistical probability that an available void will present itself to a permeating molecule more frequently in a hot system than the same system at a cooler temperature. Also, the plastic's inter-molecular voids become larger through the increased kinetic energy at elevated temperature; again enhancing the probability of a diffusing molecule to enter it.

From the statistics, it happens that absolute system temperature in degrees Kelvin and a permeation term are directly proportional; this term is the logarithm of the permeation coefficient, which in turn is the permeation rate applying to a unit cube at 1 bar pressure.

In the next section, this paper provides a sharper focus on PTFE-lined pipe and fittings and discusses different manufacturing techniques and resin characteristics.

PTFE Processing, Materials, and Methods

As mentioned above, PTFE cannot be made into useable shapes using traditional melt-processing methods. Rather, it is processed with unique, and generally very expensive, equipment. For the general shapes required for production of PTFE-lined pipe and fittings, manufacturers have several alternatives; these will be described in the coming subsections. In order to select the option or options that will be used, it should be evident that an investing manufacturer must use a calculus that includes total cost of the investment, size range and configurations to be produced, and the likely payback of the various options. On the payback side, an estimate is used of the likely market size, and how much of that market is addressable given the advantages and disadvantages of the options chosen. For maximum flexibility, a manufacturer would be capable of producing PTFE-lined piping using all of these methods. Below is a brief overview of the available methods for processing PTFE into the shapes used for plastic lined pipe and fittings.

Paste Extrusion

In this method, finely cut PTFE powder is used. PTFE powders of this texture are highly sensitive to mechanical damage and at normal room temperatures are easily "bruised". The reasons for this sensitivity are well known: thus, it is common to ship, store, and mix or blend the powder under refrigerated conditions.

Step one in the paste extrusion process is to mix a carefully measured recipe of the powder with a liquid, which serves as a lubricant. Naphtha or similar aromatic petroleum distillates are common. Some manufacturers add fillers at this step in order to impart certain desirable properties. Subsequently, the mix is sealed in containers, and allowed to age at room temperature, typically for a period of 24 hours or more, in order to improve homogeneity. Step two involves the compression of the aged mix in a vessel in order to form a billet. This step drives out air and further homogenizes the mix, as wetter, (higher pressure) areas donate lubricant to the dryer areas. In step three, the billet is placed in an extrusion chamber (at room temperature) and compressed with substantial hydraulic force such that it flows between a die and core pin disposed at one end of the chamber. The resulting extrudate has the appearance and texture of a very viscous paste, from which the general name of the process is derived. The fourth and final step is a thermal sintering process, which first drives off the lubricant and then melts the extrudate, enabling molecular coalescence and crystal growth to occur. This sintering process occurs either "in-line" with the extrusion process or in a subsequent batch process. In both cases, the temperature profile experienced by the extrudate during heat up and cool down are critical for imparting desired properties.

The general properties of paste extruded PTFE products result from the molecular orientation which occurs during the extrusion process. In this process, fibrils form and orient themselves parallel to the extrusion axis. This, in turn, results in a tendency to anisotropic mechanical properties, some of which may be undone during the coalescence that occurs during sintering. Regardless, it is considered axiomatic that paste extruded material has a degree of flexibility that is absent in materials produced using other methods. It is typical that paste extruded PTFE has a very smooth surface finish imparted by the die and core pin. Conventional wisdom holds that the small particle used to form the original mix also results in smaller voids and hence lower permeation rates compared to methods that utilize coarser granular powders; this is, however, false. (See further discussion of this topic in Appendix C).

Ram Extrusion

In the ram extrusion process, a relatively coarse, granular PTFE powder is used. It is sometimes pre-sintered to minimize the additional heat energy required to achieve coalescence and crystal growth. This, in turn, enables a relatively fast "in-line" sintering process. The process is generally continuous; the free-flowing resin is metered into a hopper positioned at the entrance to a die and core pin, around and within which, electrical heating elements are disposed. An appropriately sized "ram" is forced through the resin in the hopper, packing a small charge of the resin into the annulus between die and core pin. The ram then withdraws, the loose resin in the hopper falls by gravity back into the space vacated by the ram and then the process repeats. Each stroke of the ram advances the charge (and all previous charges) through the heated section of the die/core pin assembly, and in this way the sintering process is accomplished. As the extrudate exits the die, it encounters air, is relatively quickly "quenched," and freezes into the shape imparted by the die and core pin. This quick quench has historically resulted in rather low crystallinity of the product and given the product a poor reputation for permeation. Post extrusion thermal treatments have been developed to address this shortcoming and it is now common for ram extruded PTFE products to exhibit some of the lowest permeation rates available.

The properties of ram extruded PTFE products are randomly oriented molecular chains which results in isotropic mechanical properties; generally this is apparent to the casual observer as a stiff smooth plastic with good dimensional consistency.

Isostatic Molding

Isostatically molded PTFE is accomplished by making molds of the desired shape. In contrast to the previously described techniques, complex interior and exterior geometries are possible. A flexible bladder is disposed between the exterior and interior shape forming mold. On one side or the other of the bladder, a vacuum is drawn, causing the bladder to be forced against that mold element by atmospheric pressure. The resulting annulus between bladder and mold wall is filled again with a coarse free-flowing granular PTFE powder. The evacuated side of the bladder is

then pressurized, causing the bladder to squeeze the resin against the other tooling member. This caused the powder to pack into a near approximation of the desired shape. However, the article has very low strength at this point and must be carefully handled to avoid breakage. The molded article is typically placed into a tray, or supporting cradle, and sintered in a batch process.

The properties of isostatically molded PTFE articles are a high degree of stiffness caused by the random molecular orientation. Very accurate dimensional properties are achievable through careful tool design and filling technique. A characteristic surface roughness on the bladder side of the molded article is one common characteristic.

The above outlined processes require a heavy investment and thus appropriately equipped manufacturers are uniquely positioned to make impartial judgments of the merits and deficiencies of each of the PTFE processing techniques described above. The table below summarizes these.

Processing Technique	Pros	Cons
Paste Extrusion	<ul style="list-style-type: none"> • Lowest investment required to enter the market • Smoothest surface finish of all techniques • Relatively simple tool design and build techniques to yield net shapes • Highly flexible end products are feasible 	<ul style="list-style-type: none"> • Fine powder resin highest cost • Billet size / fragility limits extrusion length and thickness • Special shapes require post processing detrimental to many properties of the article (T&E, thickness, crystallinity) • Anisotropic mechanical properties
Ram Extrusion	<ul style="list-style-type: none"> • Minimal opportunity for green state damage • High degree of automation possible • Mid-level resin cost 	<ul style="list-style-type: none"> • Very costly high alloy tooling to resist HF • Very costly equipment/factory investment • Post extrusion thermal treatment required to improve crystallinity
Isostatic Molding	<ul style="list-style-type: none"> • Article size limited only by tooling • Batch sintering enables highly engineered thermal cycle, and property optimization • Isotropic mechanical properties • High modulus of elasticity in end products 	<ul style="list-style-type: none"> • Batch sintering required • Highest capital investment to enter market

RECENT ADVANCEMENTS

In making a thorough study of the current knowledge base of PTFE processing, and applying the results of numerous experiments, a qualified research and development team has been able to significantly advance the state of the art. Specifically, the team has developed two new methodologies and innovatively applied the statistical tool known as Design of Experiments, (DoE) and then used the results of these efforts to design a truly optimized PTFE-lined piping system. These methodologies have been developed in these areas, and will be expanded on in the following sections.

- A method which allows PTFE processors to discriminate among the many resin formulations on the market, in such a way that an assessment can be made of the **potential** of individual formulations to be processed for optimal properties.
- Rigorous conduct of carefully designed experiments to determine sintering oven profiles which will consistently deliver optimal properties.
- A method of assessing the effect of each step in the lined piping manufacturing process to determine which have a significant impact on crystallinity or the desired property of interest.

Resin Formulation Selection

There are a plethora of PTFE lined piping system options for use in producing the liners. Historically, the selection process has been made using a variety of decision factors including cost, resin manufacturer claims, processability, and perhaps most importantly, equipment availability. During the research for this paper, the team had at their disposal, equipment suitable for all three of the above described processing methods. Thus, a resin formulation selection from virtually the entire scope of product offerings was possible. This raised the difficult question of how to discriminate among them in a scientifically sound way. Ultimately, a set of analytical processes which provided a factual, numerical selection process was developed. The exact methodology is considered proprietary, but a hallmark of the process is that individual resins are subjected to a series of mini-sintering cycles and important performance indicators are assessed after each cycle. The process is continued until it becomes apparent that the resin has been over processed and the results are compared graphically to similar results for many other resin families. In this way, the researchers were able to assess the potential of many resins and make an appropriate selection.

Sintering Oven Profile Determination

The exact temperature profile to which PTFE products are exposed during sintering is the key factor affecting most physical properties, including crystallinity. Thus, it is vital that a profile be developed that produces the desired properties. Most PTFE resin manufacturers can provide some guidance on the various parameters, such as the temperature ramp rate. However, each oven has unique characteristics and peculiarities. It is the responsibility of the process designer to work with the available equipment to determine the profile. Most commonly, this has been done by trial and error. Inevitably, this results in a marginally suitable thermal cycle, but almost certainly one which is not optimized for the desired properties. However, by adopting a rigorous scientific approach to the problem, statistical techniques can be employed to derive an oven profile which provides the optimal properties sought by the designer.

Lined Pipe Assembly Method Analysis

Six Sigma methodology provides a tool to consider inputs and outputs at each process step, and then to experimentally determine the impact of varying inputs on the outputs. This is a fundamental teaching of the Six Sigma "DMAIC" process, but one which is seldom applied with discipline and resources appropriately. The designing organization has reviewed each step in the PTFE lined pipe assembly process and used the findings to modify the process to produce optimal outputs. In particular, traditional methods of achieving a liner-to-housing interference fit

have been scrutinized. Most PTFE manufacturers utilize a variant on the “Method of Lining and Jacketing Tubular Members with Prestressed PTFE” developed and patented by Resistoflex in 1962 (ref US Patent number 3,050,786). This method has made a reliable and robust assembly, but has now been shown to include a detriment to the overall permeation resistance of the assembly. Specifically, the heating and stretching of the PTFE which enables the liner to be installed in a housing smaller than the molded shape of the PTFE, does mechanical harm to the crystalline matrix of the plastic. Through careful study and experimentation, the research team developed an installation method that retains the benefits of the patented process, but avoids the detrimental effect of the pulling and stretching which damages the crystal matrices. The new process accomplishes the needed diameter reduction while simultaneously increasing density and strengthening the PTFE. The details are proprietary, but the measured crystallinity has been statistically proven to be improved during installation when the new process is employed.

“Most PTFE manufacturers utilize a variant on the process developed and patented by Resistoflex in 1962 (ref US Patent number 3,050,786).”

Accomplishments in PTFE Lined Piping Optimization – Practical Experimentation

The net results of the applied use of the above research have achieved a significant lowering of the permeation rate. This has been demonstrated using a variety of recognized permeation analysis techniques as well as through the development of revolutionary new techniques. Initial, or “alpha”, permeation testing was done using small flattened coupons cut from variously processed PTFE and PFA pipe liner samples. In this initial experiment, the coupons were fixed in such a way that one side was exposed to pressurized helium while the other side formed the bottom of a water filled graduated cylinder (see appendix A for depiction of experiment setup). This testing was performed at room temperature; some results are depicted in Illustration 1.

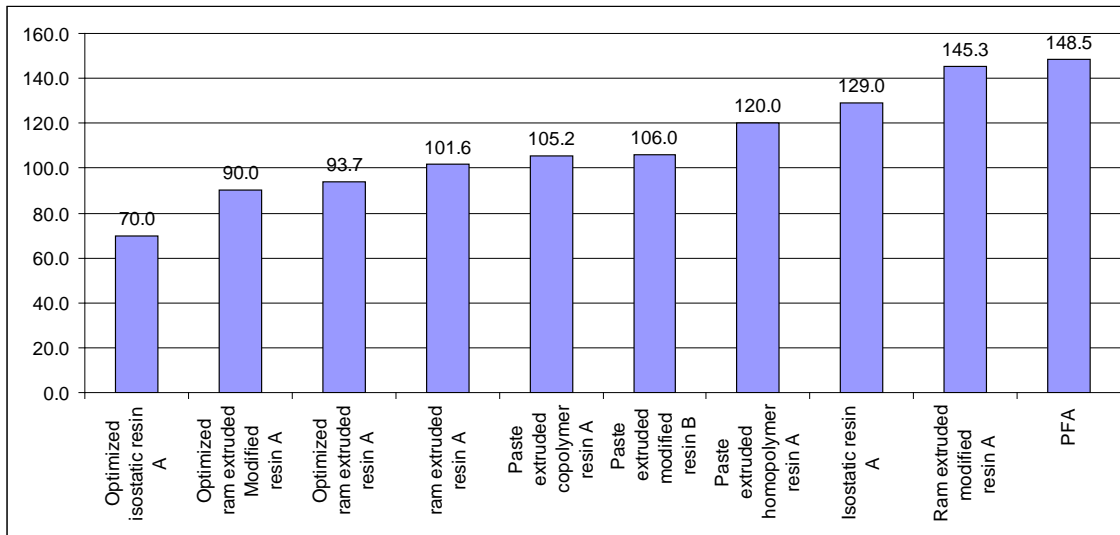


Illustration 1

The authors recognized the shortcomings of testing with small flattened coupons at room temperature. The strain imposed on the liner represents a distortion of the “free state” molecular orientation. Also, plastic-lined piping is seldom applied only at ambient temperatures. Thus, a recognized third party permeation test lab was employed to test cylindrical samples at elevated temperatures. The test facility used was Mocon Inc, in Minneapolis, MN. The cylindrical configuration is the common shape of actual lined piping samples articles. **Illustration 2** depicts

the results of this second round alpha testing. Appendix B depicts the test configuration used at Mocon.

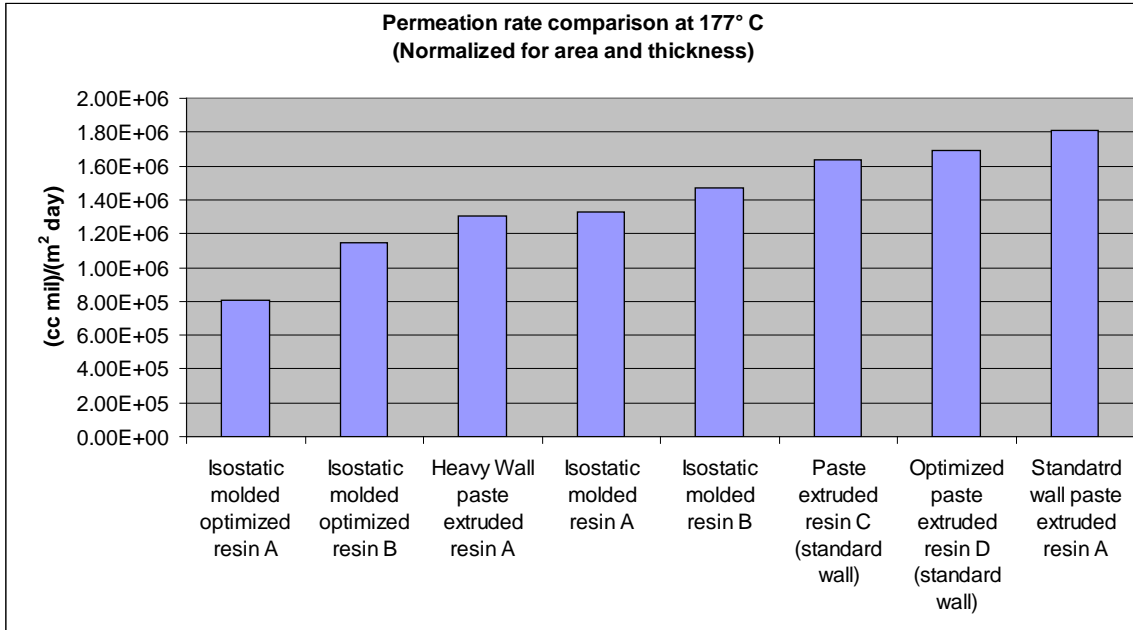


Illustration 2

Finally, the authors determined that the most valuable testing would be done with actual cylindrical pieces of pipe liner, containing known aggressive liquid permeants, at various temperatures which result in various motive vapor pressures. To date, testing has been administered with 36% hydrochloric acid solution. The testing is an ongoing effort, being conducted at the Materials Engineering Research Laboratory (MERL) in Hitchin, UK. The testing apparatus and methodology has been a joint collaborative design effort between the scientists at MERL and the research team. It is fully described in Appendix C.

The tests were conducted until a “steady state permeation rate was achieved. **Illustration 3** depicts a typical outcome of two rounds of these tests. On this graph, two bars for each liner sample type are shown. These bars represent the measured long term permeation rate of the 36% HCl solution, at both 250°F and 365°F. Thus, the liner which produced the lower bars has a lower permeation rate. Over the long term, the liner with the shorter bar, will result in less permeant available to attack the housing. Fundamentally, this will result in longer useful life for lined pipe systems before either of the above mentioned “end of life” events occur, these being significant weakening of the housing from chemical attack and liner deformation.

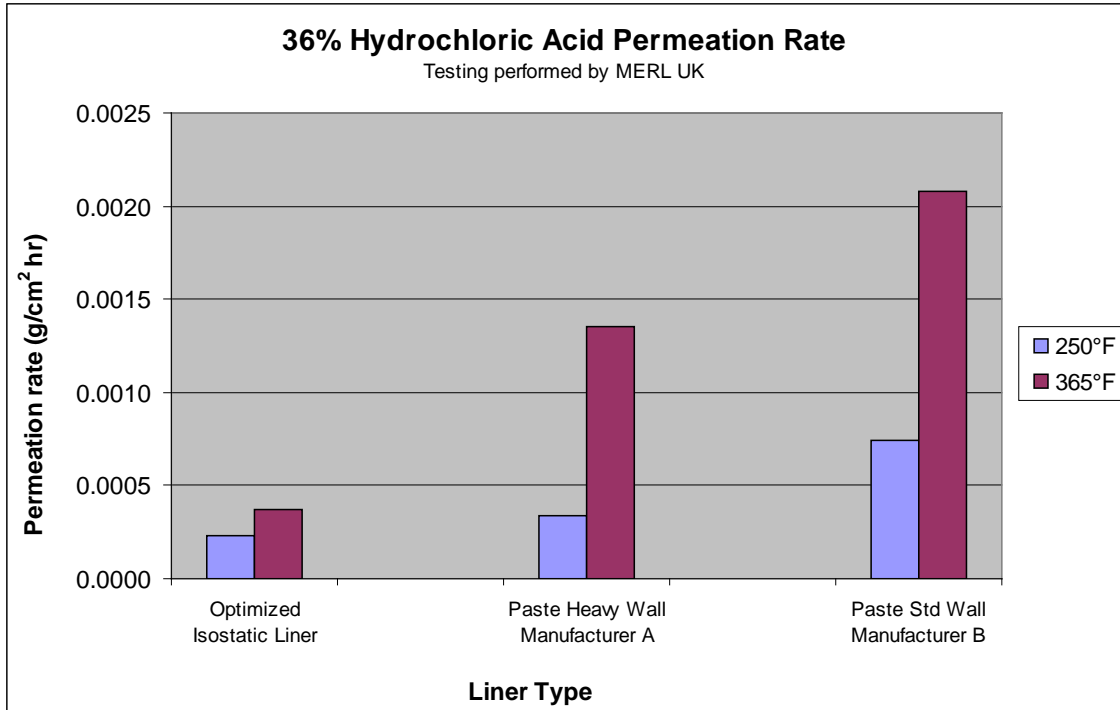


Illustration 3

CONCLUSIONS

The experimental results described above represent a new paradigm in thinking about the safety and integrity of PTFE lined piping systems. The research represents the first extended duration permeation testing done with real-world PTFE liner thicknesses, chemicals, and temperatures. Previously, conventional wisdom held that differences between the various PTFE lined piping systems in the marketplace were minor and that the manufacturing method or liner wall thickness were key factors in the performance. This research provides groundbreaking evidence that these factors are much less significant than the subtle aspects of the processing technique. More detail on the conclusions to be drawn from this research is below.

Optimization

At the outset of this research, the authors posited that PTFE liner crystallinity could be manipulated and “optimized” for performance and longevity in plastic-lined pipe intended for chemical process service. This hypothesis has been borne out. True breakthrough achievements are possible with the disciplined application of the scientific method to liner processing parameters. It is possible to produce PTFE liner with permeation rates on the order of 50% below the next best current product. Much larger gains are apparent in comparison to more typical product offerings. Furthermore, the research presented in this paper has been done with an eye to secondary metrics such as tensile strength, elongation, and density. The gains perceived are feasible without compromising these important mechanical properties. This is significant in that varying mechanical forces are commonly imposed upon all plastic liners in piping, as a result of thermal expansion differential with the metallic housing, and residual stress remaining from installation and “flaring” of the gasket surfaces. An optimized PTFE lined piping solution truly provides the full strength of the metallic outer shell, and the corrosion resistance of the PTFE liner.

Resin Discrimination

Prior to this study, it was common to see graphical comparisons of permeation rates between various fluoropolymers. Most frequently, PTFE was reported as a single rate. A key

learning of this research is that PTFE can be processed in many ways and the end result can be a wide range of permeation rates. Thus, users are advised to view claims that a given material is superior or inferior to "PTFE" with skepticism. Processing parameter adjustment and, in particular, sintering oven profile variation can produce widely varying results. A careful consumer of PTFE line piping products will attempt to discern the level of expertise in the factors discussed in this paper from their supplier of choice. Familiarity with the potential gains of careful oven profile development should provide users a level of enhanced confidence in vendor selection.

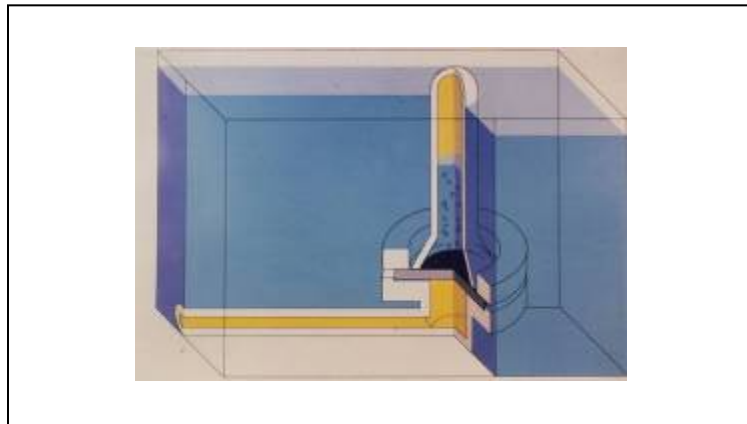
Factors Affecting Permeation Rate

In general, the factors affecting permeation have been widely understood. Less well understood are the relative weights of these factors. This study has shed new light on the importance of crystallinity as a factor. Conventional plastic-lined piping wisdom held that PTFE wall thickness is of primary importance in the area of permeation rate. If polled for a secondary factor, industry participants would site a variety of others, including raw resin grain size, surface finish, system temperature, and possibly crystallinity. This research has resulted in proof that crystallinity is clearly of primary importance. Although not reported in the data in this paper, wall thickness has been confirmed as an important contributor to permeation rate. End users are advised to weigh these factors and the manufacturer's comfort level with the impact in their buying decisions.

Test Rig Development

The project provided a significant education in the design of permeation test cells. Dozens of design iterations were tested before arriving at a design which was capable of withstanding the forces of the real-world conditions under which the liners were evaluated without leakage or deformation. Under these conditions, mechanical seals were found to be universally unusable for unreinforced PTFE liner testing. Even the outer pressure retaining vessel required extensive development in order to arrive at a design capable of sealing and which did not contribute experimental noise in the form of corrosive interactions with the permeant species. The end result is a new standard in the realm of permeation testing of thick walled cylindrical plastic forms. The design depicted in Appendix D is schematic in nature and not intended to divulge the actual form of the test rig. The author considers this a proprietary development.

Appendix A – CRANE ChemPharma Flow Solutions Internal Alpha Permeation Testing



Appendix B – Mocon Inc Beta Permeation Testing



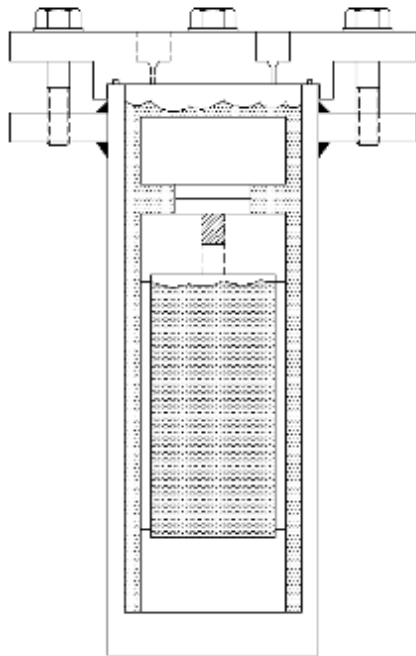
Appendix B1 – Mocon Scientist Credentials

The testing was performed by J. Georgia Gu.

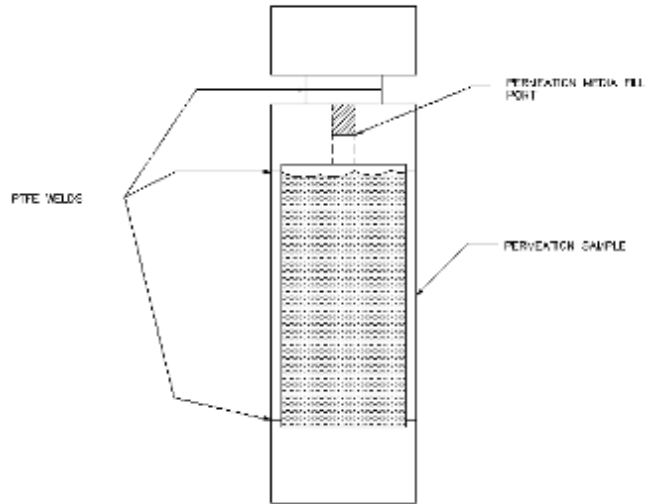
Ms. Gu holds the **Master of Science in Packaging** degree from Michigan State University, East Lansing, Michigan, USA, as well as **Master of Science in Chemistry** and **Bachelor of Science in Chemistry**, 1984 from Fudan University, Shanghai, China. She has worked as senior scientist at Mocon since 1997. Prior to that, Ms. Gu held teaching and research positions at both Michigan State and East China University of Science and Technology. She is a member of both the Institute of Packaging Professionals and the International Society of Pharmaceutical Engineering.

Appendix C – Materials Engineering Research Laboratory (MERL) Gamma Testing

PERMEATION TEST VESSEL,
WITH PERMEATION CELL
SUBMERGED IN WATER



SOLID PERMEATION TEST
CELL PARTIALLY FILLED
WITH LIQUID MEDIA



Appendix C1 - MERL Scientist Credentials

The testing was performed or overseen by Doctors Robert (Bob) Campion and Nickie Smith.

Dr. Robert Campion BSc, PhD, CEng, FIMMM

Dr. Campion is an author of more than 50 scientific and technical publications on elastomers, thermoplastics, cured rubber/metal & rubber/rubber bonding, auto adhesive tack, rubber compounding, polymer durability in fluids, and high pressure gas permeation and diffusion. Previously a senior member of the scientific staff at Dunlop Research Centre/Technology Division for 25 years, Dr. Campion subsequently served a period at MRPRA. He also served as Committee member of the Polymer Science Group of the Institute of Materials (IOM) and Chairman of IOM Polymers in Extreme Environments conferences. Special research interests, normally applied to the Offshore Oil Production or Automotive industries, include high pressure gas permeation & diffusion through elastomers and thermoplastics, fuel permeation, fluid/polymer compatibility & ageing issues, polymer structure/property relationships, novel compounding approaches, and adhesion bonding.

Dr. Nickie Smith BSc, PhD Chemical Engineering (Polymers)

Dr. Smith is a senior scientist with a chemical physics background and expertise in structure property relationships in polymer blends; project manager for wide range of single client commercial projects relating to materials selection, development and evaluation, chemical ageing, life prediction and durability of polymeric materials. Research interests include development of accelerated test methodologies to determine low permeation rates in automotive fuel systems. Collaborated on a wide range of UK government and European Commission funded research projects relating to the development of new materials and their evaluation.

Appendix D - Void content analysis of paste extruded PTFE and Optimally Sintered Isostatic PTFE

The Scanning electron micrographs below, taken at 15,000X magnification, depict typical void content of common paste extruded PTFE pipe liner, and optimally sintered isostatically molded PTFE pipe liner. Illustration D1 is optimally sintered isostatic liner, and illustration D2 is paste extruded liner.

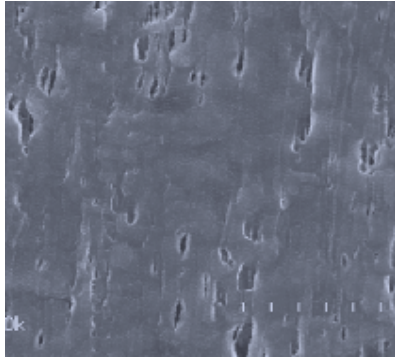


Illustration D1

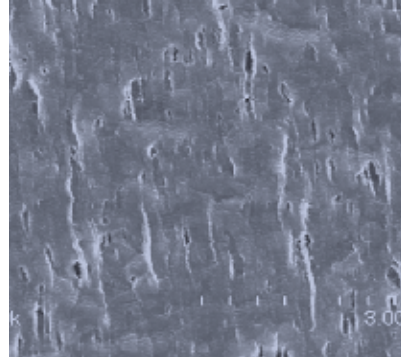


Illustration D2

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