CHANGES IN PVDF TO IMPROVE HIGH-PURITY WATER PIPING SYSTEMS

In the initial years of the development of semiconductor technologies, the manufacturers found that the quality of the water in the wafer rinse process was critical to the performance of the computer chips. In the 1980s, it was generally considered that chip yields of 75% were considered common for a start-up manufacturing plant (1). These low yields were found to be partly associated with materials of construction in the process fluid handling system used for cleaning the silicon wafers.

The original systems were made from steel pipes and the high ionic extractables related to metals proved to give less than perfect performance for the produced chips. A move to plastic piping ensued, and for a short period of time this was found to reduce metal contamination, but then led to new forms of contamination such as total organic carbon (TOC) and residual extractables related to the processing aids, stabilizers, and other additives common to commodity plastic piping. An additional concern about commodity plastic piping was that these materials were not optimal for higher temperatures, which obviously allowed for improved cleaning performance.

Early Movement to PVDF

Polyvinylidene fluoride (PVDF) was being tested by some of the first engineering pioneers in the design of high purity piping systems maybe as early as 1980 (2-4). From the data that was being developed, it was very clear that the use of PVDF was a potential game changer in the semiconductor high-purity water processing industry. Unlike other polymers that were used for water at the time, PVDF was naturally stable and did not need the addition of light stabilizers, pigments, and processing aids to be made into a smooth surface extruded or molded product that maintained its initial properties for a lifetime of use (5, 6).

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In addition, this was a material commonly used in tough chemical applications such as strong acids, chlorinated solutions, and hydrocarbons in service temperatures up to 145°C since 1965. Hot or cold water posed very little issue for this specialty polymer that previously was well known in niche applications such as the nuclear reclamation industry, pulp and paper, bromine, chlor-alkali, and petrochemical industries. Piping, valves, pumps, tower packing, filtration equipment, and tanks already existed commercially to service these other industries (7).

The initial PVDF piping systems considered for the processing of high-purity water were based on these existing designs that were popular for applications where a difficult chemical had to be moved from place to place and, more importantly, contained. These systems were joined by methods that today would be considered archaic by the current high-purity industry standards. Systems like flanged plastic lined steel, socket fused solid piping, and butt fusion joining were very common, and used on some rather large jobs.

Figures 1 and 2 shows examples of butt

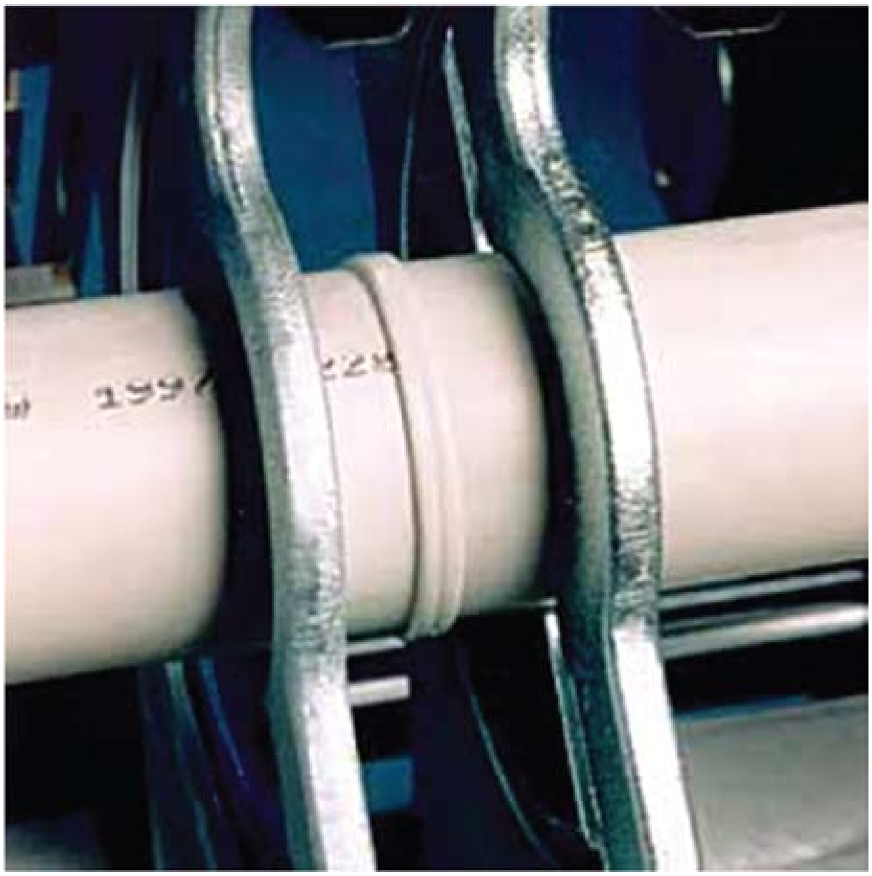

Figure 1. An example of butt-fused plastic piping.

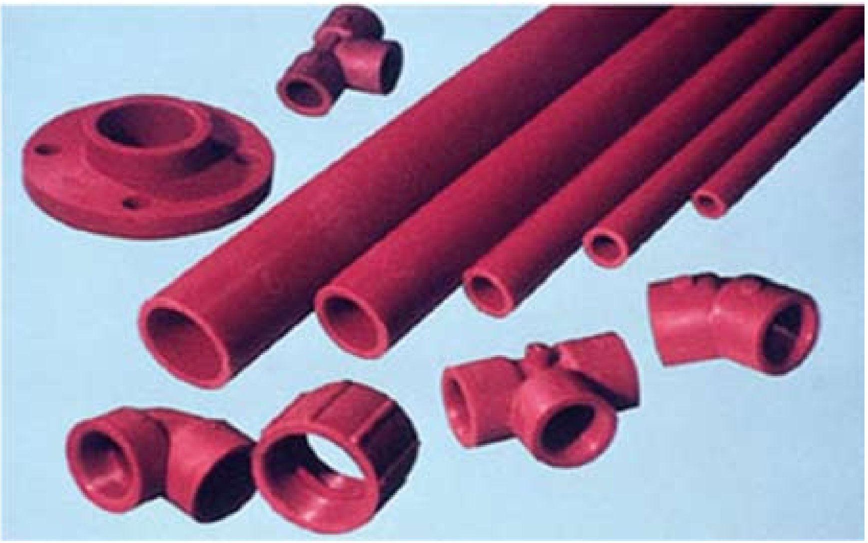

Figure 2. View of plastic fittings designed for socket fusion and flange style joining.

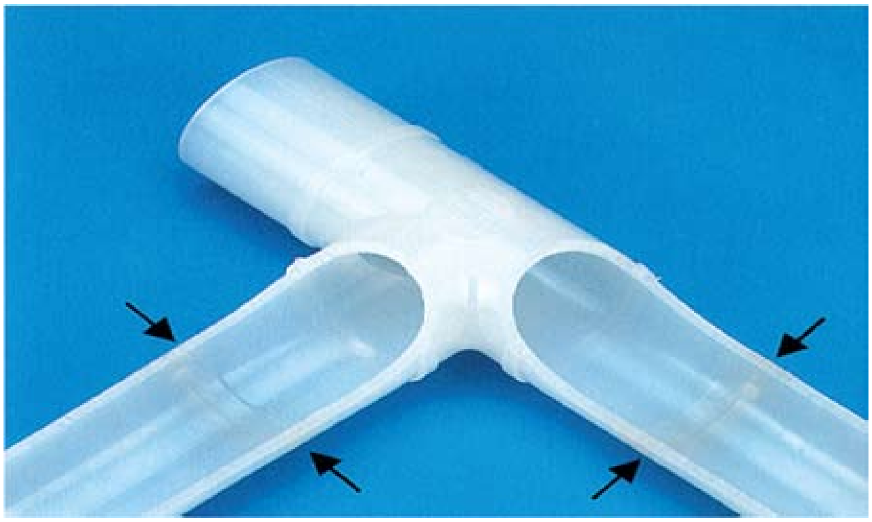

Figure 3. Example of beadless welding of PVDF.

Figure 4. Vessel made from a welded PVDF sheet,

fusion and socket fusion systems. Each of these joining methods posed a potential of some sort of location conducive to bacteria buildup. As nearly all systems in the early stages were ambient water, the first joining methods for PVDF pipe led to the need for frequent sterilization, which reduced the overall efficiency of the chip manufacturing process.

At this time in the 1980s, the industry was benefitting from finding a very pure and robust material to process pure water. From the data being developed, it was unquestionable from a starting point that PVDF was very low in water-related extractables as a polymer of construction, but work was needed on the mechanical design of the fluid handling systems to meet the needs of this fast growing industry at the time (8, 9).

New Pipe Joining Methods

In the late 1980s, a novel way to mechanically join piping that was originally designed for food, drug and beverage markets came on the scene with PVDF as one of its major available materials of construction. "Sanitary" PVDF piping offered a way to join plastic systems in an improved manner versus flanged systems.

The sanitary system was lighter than plastic-lined steel, and gave the user an option to never have to throw away a fitting or pipe that had been welded poorly. These systems gained some popularity that still stays today in small laboratories, but ultimately was found to be suspect when the outside diameter (OD) of the piping was increased above 2.5 inches. The reasons for this, is that the plastic could be deformed in long runs of piping due to expansion and contraction with any appreciable heat variation.

This short period of discovery led to better ideas on how to improve upon standard contact butt-fusion systems that were competing with the sanitary concept at the time. Sanitary systems remain in use but for smaller or very specific applications for PVDF in laboratories. Two types of new joining methods arose from the existing array of options:

Beadless fusion, which was an innovative method of welding that when perfected, makes a pipe appear to have no weld line at all on the inside surface.

Figure 5. Example of ASTM E84 (25/50) compliant pipe in a construction floor space.

Figure 6. The biotech industry is moving to polymer-based disposable systems to reduce capital costs and ensure optimum system performance.

This type of welded joint takes time to make, but the suppliers of the welding apparatus have created a machine that is very consistent and largely free of human error when instructions are properly followed. As would be expected, this type of weld can be highly desired in the pharmaceutical water and light chemical process. For large semiconductor plants, there is a desire for a faster and easier joining process. Figure 3 shows the smooth inside of the joints in a beadless weld system.

Infrared welding (IR), which is method of welding where the contractor has a very well controlled machine that emits heat without contact of each area of a piping system that will be joined together. This may sound like a minor issue, but standard butt fusion has a wide window of operator skill that can create a weld of varying bead formation. Additionally, in contact welding, it is the case that materials can stick to the heater plate and cause unwanted material geometry and contamination in the weld area. IR welding eliminates many of the aspects of error than can come with butt fusion that in many end uses for a high performance pipe would not be a big concern.

Since its inception in the early 1990s, the years of development of joining systems has led to IR welding being the most popular choice by the most well-known semiconductor manufacturing facilities

Progression of PVDF in High-Purity Water

In 1980, about the time that PVDF was being developed for use in high-purity water, most PVDF piping systems were pigmented either in red, blue, black, or green just to distinguish in a chemical plant from other polymers like polypropylene, PVDC, and polytetrafluoroethylene (PTFE). To the untrained plastic pipe user, many of these polymers look the same and the use of color prevented a less sophisticated user base from accidentally putting a material in 130^{o}C service and having a disaster occur. It was a simple process to no longer add pigment to the PVDF and sell a "natural" product to the new group of engineers designing high-purity piping systems for the semiconductor industry.

Initially the only offering from PVDF suppliers for piping systems was in the form of homopolymers of vinylidene fluoride, and as such, a limited amount of grades that could be used for pipe and fittings. A large amount of research was generated in the 1980s that led to grades of PVDF that gave the optimum in surface smoothness in extrusion, and effective surface finish and cycle time in molding.

In the 1990s, manufacturers created a

process that allowed the in-line deionized (DI) water washing of PVDF emulsion in the reacted latex form when the material is still at its smallest particle size before being processed into a pellet that is then sold to the component manufacturers to make pipes, pumps, valves, filtration equipment, instrumentation, and tanks. This was a great achievement because coupling this with the newer joining technologies by the pipe manufacturers, the enduser now had an even more pure product to the parts per billion (ppb) extraction levels along with a piping system that minimized bacteria growth areas (10). To this date since the mid 1990s, the grades for the most popular high-purity PVDF piping systems have not changed and they continue to provide excellent service performance.

As PVDF homopolymers continued to perform at the levels desired in hot and cold high-purity water piping systems, engineers began looking at other uses for PVDF-type chemistry in areas where more expensive materials were being used to ensure water purity. PVDF copolymers of vinylidene fluoride (VF2) and hexafluoropropylene have gained popularity in the area of flexible tubing (11). PVDF homopolymers are well known for their high strength across a broad temperature range, which makes them a very good piping material (12). For tubing, the opposite is needed and the addition of comonomer to the polymer backbone creates a break up of crystallinity of the polymer which results in a material with greater flexibility.

Purity is not lost because of the comonomer being fully fluorinated (and thus very stable) and the amount of flexibility can be varied based on the need of the user (13). To put it in perspective, the flexural modulus of the PVDF homopolymer can be generalized at about 2,070 mega pascal (MPa) (plus or minus, depending on the molecular weight distribution) and PVDF copolymers are commercially available in high purity versions down to 200 MPa. Table A lists some commercial versions of PVDF and PVDF copolymers:

PVDF Copolymers

While the rigidity of the PVDF homopolymer is desired for piping system design, the more flexible PVDF copolymer is often desired for the construction of tanks and tank linings which are components often subjected to high welding and bend stresses (14). In this case, the support of a metal or fiber reinforced plastic (FRP) backing allows an economical use of thinner PVDF linings that are in contact with high-purity water. Since PVDF and PVDF copolymers are very good barriers to water, the lining thickness can be as low as 1.5 millimeters (mm) (60 mils), and still provide adequate permeation resistance to avoid the extractables that would be associated with the substrate. This combination of PVDF being the strongest commercially available fluoropolymer up to 140°C (15) and being available as a highly flexible fluoropolymer within the same manufacturing process makes this a very special polymer for engineering design. High temperature capable fluoropolymers of varying performance, flexibility range, and molecular design, cannot be welded to each other, except for PVDF (16). Figure 4 shows how a high-purity tank is fabricated using fabric backed PVDF copolymer sheets welded and adhered to an existing metallic shell.

Endusers of PVDF in Pure Water

As discussed in several paragraphs of this article and confirmed in a multitude of other published articles, there is a very high use of PVDF in the semiconductor industry (17). From the development of semiconductor-based technologies and the increasing desire for improved processes in the biopharma and potable water industries, many specifications at major engineering firms have come to prefer PVDF over metals or other commodity polymer options in the design of all types of pure water systems (18, 19).

In the biopharma industry there are standards adopted by ASME-BPE (20) that clearly helps assist designers on what to consider when using a PVDF piping system. As it relates to potable water, many PVDF grades are listed to NSF 61, which is the testing and listing protocol defined by the National Sanitation Foundation. To obtain the specific grades of PVDF and PVDF copolymer that meet this listing one can go onto the NSF.org website.

The reason that PVDF is chosen in these industries compared to the low extractable concerns in the semiconductor industry is that along with being a pure material that complies with regulatory compliance, PVDF can be steam cleaned (21), stands up to cleaning agents in a higher performing manner than stainless steel, and offers a light weight, easily installed option. This is coupled with the fact that some forms of high-purity PVDF comply with the ASTM E84 (25/50) criteria required in building codes for fire safe products (22). Figure 5 shows examples of ASTM E84 code compliant piping installed in an institutional building.

Use of PVDF in biotech applications has more than tripled globally since 2003. Use in potable water applications where PVDF is bonded to polyethylene in residential housing construction in Europe is experiencing double- and triple-digit growth for the last 3 years. It is estimated that composite PVDF/PE structures can last 5 to 10 times longer than solid PE or PEX structures when chloride disinfectants are used.

New Applications for PVDF

One of the more exciting developments of PVDF in the last 10 years has been its use in filtration products. Flat sheet PVDF membranes had existed for years and are highly used in the biotech industry and semiconductor industry (23). Newer versions of PVDF and PVDF copolymers lend themselves to hollow-fiber membrane production for the purification of water on a global basis.

In addition to this development, very fine fibers of PVDF can be extruded to produce woven and non-woven fabrics that can be combined in filtration devices for ultimate performance in water applications where disinfectant resistance, high temperature and overall general long life are desired from a material. This use of PVDF is now commercial, but there is much room for development and it is perhaps the most exciting new technology platform being pursued at this time.

The acceleration of the development of fabrics made from PVDF will hopefully fill the void that has existed for a very long time where filtration component designers were forced to use dissimilar

TABLE A
Flexibility and Melt Point of a Few PVDF Resins

PVDF Resin Grade	*Tensile Strength at Yield MPa (psig)*	*Flexural Modulus MPa (psig)*	*Melting Point ºC*
PVDF Hhomopolymer	52 (7,500)	2,070 (300,000)	168
PVDF Copolymer A	40 (5,500)	1,200 (170,000)	158
PVDF Copolymer B	28 (4,000)	700 (100,000)	143
PVDF Copolymer C	21 (3,000)	400 (60,000)	136
PVDF Copolymer D	17 (2,500)	200 (30,000)	123

materials in the construction of the final products. It was common to see PVDF filters with polyolefin supports that did not possess the temperature or chemical resistance of PVDF, or PVDF filters supported by much more expensive materials than if the entire structure was made with the much more affordable PVDF polymer (24-26).

Another application is composite disposable systems for biotech fluids. Pure and flexible PVDF copolymers can be bonded in multilayer structures with other very flexible substrates like thermoplastic urethane (TPU), polyether block amide, and flexible polyesters. These multilayer structures can be any structure that is extruded and this technology is commonly seen in tubes or films that are made into bags (27). Figure 6 shows an example of the use of PVDF multilayer films as a disposable system.

Summary

PVDF emerged into the high-purity water scene in the 1980s. The original products, and methods of joining the products, have all evolved in ways that improve the overall quality of high-purity water. As with many technology roadmaps, PVDF components arrived to the semiconductor industry with designs appropriate at that time to support other less technologically advanced industries. These designs and polymers have been further adopted for specific use in the semiconductor industry, which has led to product developments fostering adjacent growth to new types of high-purity water industries such as biotech, pharmaceutical, and potable water. The developments continue, and it is highly likely that endusers and designers across many seemingly unrelated industries will reap the benefits in cost, performance, and system availability from the suppliers of PVDF components.❑

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