The Application of PVDF in Converter Cooling Pipeline

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Abstract. The structure, mechanical property, thermodynamics property, electrical aspects, radiation property and chemical property were introduced, and PVDF could satisfy the requirement of converter cooling pipe. PVDF department and pipe of distribution pipeline of converter cooling system in Debao HVDC project are used to introduce the molding process of PVDF.

1. Introduction
Converter valve is the core equipment in HVDC project. Converter valve is made up of thyristor, damping capacity, voltage sharing capacitor, damping resistance, equal resistance, saturable reactor, control unit of thyristor and so on. The converter valve cooling system is one of the key system in HVDC project. The cooling system let the heat emission of each component to the outdoor environment, which could ensure that each component of the converter valve works under normal temperature. The converter valve cooling system includes main cycle system, water quality purification system, compress-stability system, outer cooling system, control system, accessory system, and water distribution system, the water distribution is the important connect channel between converter valve and converter valve cooling system, so the material of water distribution requires high reliability.

PVDF resin possess the character of both fluororesin and general resin. In addition to favorable chemical resistance, heat-resisting quantity, oxidative resistance, weather fastness, resistance to ray radiation, it also has favorable piezoelectricity, dielectric property, pyroelectricity and other special property. The appearance of PVDF is translucence/white powder or particle, the molecular chain of PVDF closely spaced, as well as strong hydrogen bond. Compare with other plastic, PVDF is quite pure polymer, it does not contain the UV stabilizer, heat stabilizer, softener, lubricant, fire retardant and fire retardant. Because of these characteristic, PVDF is suitable for the transmission of ultrapure water and chemical agent in semiconductor industry. PVDF hardly react with any medium, because of its chemical inertness, so PVDF is a better choice for water distribution pipe.

At present, HVDC project use imported technology including water distribution pipe, the lead time is too long and after-sale is relative lag, so how to use PVDF to manufacture the water distribution pipe of converter valve become the hot research area[4-5].

2. The property of PVDF

2.1. Physics property
The C-F bond distance in the PVDF molecule chain is 0.317nm, the bond energy is 486kJ/mol, which is the same with the general resin, so it has favorable heat-resisting and chemical proofing property, and its melting temperature and thermal decomposition temperature have large difference, and has favourable
processability, so PVDF is easy to process using many forming methods. The glass transition temperature of PVDF is low to -35℃, and present dispersedness under 70℃, so PVDF has the favourable property of impact resistance and high distortion temperature.

2.2. Mechanical property
Because of the high polarity of PVDF molecule, it has better mechanical strength in fluoropolymer, the tensile strength of PVDF reaches to 55Mpa under room temperature and 35Mpa under 100℃. The tensile creep quantity is only 2% after 1000h under 21Mpa loading and room temperature. From table1 and table2, we can see that the hardness of PVDF ranks only second to hard PVC, the abrasion value ranks only above PA66, so both the hardness and abrasion value are relatively optimal.

| Plastic   | HRC  | Shore |
|-----------|------|-------|
| PVDF      | 110  | 86    |
| PCTFE     | 110  | 85    |
| PTFE      | 20   | 55    |
| FEP       | 25   | 55    |
| ETFE      | 50   | 75    |
| PFA       | -    | 60    |
| PP        | 85-110 | -     |
| Hard PVC  | 115  | 90    |
| PA66      | 110  | -     |

| Plastic        | abrasion value(1000times)/cm³ |
|----------------|-------------------------------|
| PVDF           | 0.0046                        |
| PCTFE          | 0.0174                        |
| PTFE           | 0.0047                        |
| FEP            | 0.0091                        |
| ETFE           | 0.0092                        |
| PFA            | 0.0057                        |
| PP             | 0.0162                        |
| Hard PVC       | 0.0089                        |
| PA66           | 0.0041                        |
| PC             | 0.0072                        |

2.3. Thermal properties
The melting point of PVDF is 170〜178℃, thermal decomposition temperature is 350℃, it crystallize rapidly when cooling to 140℃. The actual suitable temperature of PVDF is -40〜150℃, so PVDF has better thermal adaption.  

2.4. Electrical properties
PVDF has the largest polarity during high polymer because of its molecular structure, the electric moment of —CF₂— is 5.3×10⁻³⁰C.m and —CH₂— is 1.7×10⁻³⁰C.m, and the electric moment of the forming molecular is 7.0×10⁻³⁰C.m, so PVDF is suitable for high insulation medium.  

2.4. Radiance properties
PVDF has strong resistance to radiation and high energy electron line radiation, the PVDF film of 100µm still maintains hot strength of 60Mpa and elongation of 30% after exposed to radiation of 100kGy in the air or N₂. The PVDF has the breakage of molecular chain and the produce of cross-linked structure when in high energy ray radiation, which is the main reason of its high radiation resistant
properties.

2.5. Chemical properties
PVDF is the crystalline thermoplastic resin, and has less porosity after film-forming, so chemical agent is hard to penetration. From table 3 we could see that PVDF has 20 years of weather aging life and from table 4 we could see the artificial accelerated aging test. The limited oxygen index is 43.7% and has self-extinguishment property, the flame retardant property reaches the UL94 V-0 level.

| Tab.3 The outdoor aging test of PVDF |
|-------------------------------------|
| **Polyme r** | Thickness/µm | Measuring Item | Exposure days |
| PVDF | 13 | Tensile strength /MPa | 0 | 564 | 96 | 2115 |
| PVDF | 13 | Elongation /% | 170 | 170 | 75 | 70 |
| PVF | 13.5 | Tensile strength /MPa | 145 | 92 | 78 | 80 |
| PVF | 13.5 | Elongation /% | 160 | 85 | 36 | 40 |
| PET | 12 | Tensile strength /MPa | 220 | After 150 | - | - |
| PET | 12 | Elongation /% | 188 | embrittlement |

| Tab.4 Artificial accelerated aging test of PVDF |
|-----------------------------------------------|
| **Example** | Thick/µm | Measuring Item | Exposure days |
| PVDF | 35 | Tensile strength /MPa | 0 | 0 | 0 | 0 |
| PVDF | 35 | Elongation /% | 235 | 236 | 234 | 230 | 207 |
| PVF | 25 | Tensile strength /MPa | 111 | 111 | 95 | 91 | 72 |
| PVF | 25 | Elongation /% | 155 | 150 | 168 | 155 | 97 |
| Soft PVC | 100 | Tensile strength /MPa | 35 | 32 | 29 | 25 | 40 |
| Soft PVC | 100 | Elongation /% | 445 | 402 | 401 | 86 | 5 |

3. PVDF forming process

3.1. The hot bending forming process of PVDF
The ratio of shrinkage of PVDF is 2%~2.2%, the products have high shrinkage when forming, so secondary machining allowance should obligate when design the large size plastic mold. Exhaust system should be reasonable designed in the plastic mold, otherwise, air vent would form inner the products because of die while of the plastic mold, and at the same time, the plastic mold should be heated when inject mold, and in order to ensure the stability of the products, the temperature should be controlled between 50~65°C. Fig.1 shows the injection molding PVDF, and Fig.2 shows the PVDF standard pipe.
3.2 The hot bending forming process of PVDF

The converter valve has complex structure, its distributing pipe line has more standards and forms. The softening temperature of PVDF pipe is about 150℃, the kinds pipe of valve cooling system distributing pipe could be made by the hot bending forming process. The PVDF pipe could be roll bent, moulded bending forming after 20~45min heating under 155~165℃, the forming size can completely meet the design technical requirements.

The large aperture PVDF bending forming process is according to the following steps:

1. Cut stock according to technological requirement and jig process hole on the pipe, wash the pipe using the clear water and wash internal and external surfaces using alcohol after air drying;
2. Put the PVDF and the flexible filling body in the 170℃ oven and heat 30min, and turn the PVDF tubing in 90 degree every 1 min;
3. Put the filling agent into the PVDF pipe and heating at a temperature of 165℃, and overturn 90 at every 1min, meanwhile fit the forming mould in the automatic bending equipment, and put the forming mould into the oven and heating at a temperature 165℃;
4. Rolling and bending to the pipes using automatic bending equipment, after bending, keep warm in the oven at a temperature of 150℃ for 1h;
5. Open the oven and cool using water or wind, when the temperature of the forming mould reaches 35℃, take the filling out;
6. Continue to cool the forming mould, when the temperature of the forming mould reaches 35℃, loosen the mould, and take the shaping PVDF pipes.

Cut off the heavy calibre PVDF pipe at any position, pick up 8 points at the fracture surface of the pipe and measure the wall thickness using callipers Δe≤0.3mm, cascade the bending pipes into a heatable circulating water circuit become a closed cycle system, the medium is pure water, the temperature of the water is 95-100℃, the water pressure is 1.15Mpa, the cycling time is 200h, the bending pipes should have no leakage, abnormal deformation and fracture.

The small aperture PVDF bending forming process is according to the following steps:

1. Cut stock according to technological requirement;
2. Put the PVDF tubings, support and the flexible filling body in the 170-175℃ oven and heat 30-35min, forming mould as also, when half the heating time, turn round the PVDF tubing and overturn 180°and continue to heat;
3. Put the filling agent into the PVDF pipe and heating at a temperature of 170-175℃ for 3-4min;
4. Take out the forming mould first 1min before take out the PVDF tubings, and fit the forming mould on the press machine, second put the PVDF tubings with flexible filling body on the mold groove, close the mold, the tubing could brake forming in the mold, and then put the mold with PVDF tubings in the oven at 170℃ for 1h;
5. Open the oven, pull out the inside flexible filling body, cold the curving PVDF pipe to 40℃ naturally and take it out, then immerse it in the water and last get the finished products.
Cut off the small calibre PVDF pipe at any position, pick up 8 points at the fracture surface of the pipe and measure the wall thickness using callipers, Δe≤0.3mm shows excellent control effect, fig.4 is the finished products of small aperture PVDF.

![Fig.3 The large aperture PVDF bending pipe](image1)
![Fig.4 The small aperture PVDF bending pipes](image2)

3.3. The welding process of pipe

The PVDF pipe, pipe fitting could butt welding using infrared welding technology, the technological process shows in the fig.6, using infrared welding technology, the parts keep clear of the heat source, it is a big improvement to the butt welding technology. The pipe end heat using radiant heat energy, the advantage of keeping clear of the heat source is making the smallest welding size, eliminating the pollution brought in by heating element and getting more straight weldings, so the bacteria has smaller growth area. Compare to the traditional heating elements, infrared welding technology could save 70% time. During the whole welding process, the temperature, pressure, time are automatically controlled and recorded by computer program, welding system and process could trace completely, any deviation will be recorded immediately and showed at the welding machine computer. The tensile, cold bend of the welding using infrared welding technology could meet the requirement. The fig.7 is the value of PVDF parts, the welding pipes of DEBAO HVDC water cooling system water transport and distribution system.

| Items                  | Value           |
|------------------------|-----------------|
| Sample size(mm)        | Ф40×2.4         |
| Sample area(mm³)       | 283.50          |
| Max force(KN)          | 21.9            |
| Strength of extension(MPa) | 77              |
| Fracture location      | Welding line    |
| Cold bend(180°)        | Non-crack       |

4. Epilogue

The thermal properties, electrical property, chemical properties of the PVDF could meet the requirement of HVDC water cooling system water transport and distribution system. Choosing injection moulding, shaping with hot bending, infrared welding process according to the structural features to realize the production of transport and distribution system.

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