PVDF and Its Copolymers & Terpolymers: Compositions & Molecular Weight
A Review of Commercial Polar Fluoropolymers

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1. Fluoropolymers that contain VDF (vinylidene difluoride) monomer are usually have dielectric constant, even the content is less than 50 wt%.

2. There are over fifty different grades of VDF-containing commercial polymers and the manufacturers usually use a name code as the grade number. It is very difficult to understand what is the exact composition (even what kinds of copolymer chemistry).

3. In addition, most of them provide the melt flow index (MFI) and not the molecular weight by GPC.

4. During the past 14 years, we have collected many commercial PVDF-based copolymers to evaluate their dielectric and ferroelectric behavior.

5. We have also produced films by either melt extrusion or solvent casting, with or without orientation.

6. New less-known fluoropolymers are also studied.
1. PVDF homopolymers with different molecular weight (MFI) produced by either suspension polymerization or emulsion polymerization.

2. P(VDF-HFP) (hexafluoropropylene) copolymers with five different compositions (medium molecular weight).

3. P(VDF-CTFE) (chlorotrifluoroethylene) copolymers with five different compositions.

4. P(VDF-TFE) (tetrafluoroethylene) copolymers with four different compositions (combining PVDF and PTFE, quite interesting behavior).

5. P(TFE-HFP-VDF) terpolymers with high optical transparency.

6. P(VDF-TrFE) copolymers with seven different compositions: ferroelectric polymers.

7. High dielectric constant terpolymer (K = 20 ~50): P(VDF-TrFE-CFE) and P(VDF-TrFE-CTFE) terpolymers invented by Penn State University

8. Fluoropolymer thermoplastic elastomer (physical crosslinking)

9. Chemically crosslinkable fluoropolymers
1. Very high molecular weight such as Solef 6020 and Kynar Flex HSV900: as binder for lithium ion batteries.

2. Medium high Mw for film extrusion and molding such as Solef 1010 or Kynar 740

3. Medium low Mw for injection molding and extrusion, such as Solef 1008, 6008, 9009, or Kynar 720

4. Very low molecular weight for multi filament extrusion, electrospinning, such as Solef 1006 or Kynar 706

5. Mw affect the crystallinity and ductility

6. Polymerization process (temperature, emulsion or suspension) determines the side chain branch and other chain defects, therefore determines the crystallinity and melting temperature. It is hard to know this as every resin producer claims they have the best PVDF resin.
# PVDF Homopolymer: Mw vs MFI

## Average MFIs at 230°C (446°F) under different loads

<table>
<thead>
<tr>
<th>PVDF grades</th>
<th>Average melt flow indices (MFI) at 230°C (446°F) in g/10 min under a load of</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.16 kg</td>
</tr>
<tr>
<td><strong>Solef® resins</strong></td>
<td></td>
</tr>
<tr>
<td>1006</td>
<td>40</td>
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<tr>
<td>1008, 6008, 11008, 21508</td>
<td>8</td>
</tr>
<tr>
<td>31008/0003, 31508/0003</td>
<td>5</td>
</tr>
<tr>
<td>1010, 6010, 11010, 21510</td>
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<tr>
<td>1012, 6012</td>
<td>0,5</td>
</tr>
<tr>
<td>60512</td>
<td>-</td>
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<tr>
<td><strong>Solef® compounds</strong></td>
<td></td>
</tr>
<tr>
<td>3108/0903</td>
<td>1,5</td>
</tr>
<tr>
<td>3208/0150</td>
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<tr>
<td>3410/0905</td>
<td>2</td>
</tr>
<tr>
<td>8808/0902</td>
<td>3</td>
</tr>
<tr>
<td><strong>Hylar® resins</strong></td>
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<tr>
<td>460</td>
<td>-</td>
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<tr>
<td>SN</td>
<td>45</td>
</tr>
<tr>
<td>20808</td>
<td>-</td>
</tr>
<tr>
<td>21508</td>
<td>-</td>
</tr>
</tbody>
</table>

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### PVDF Homopolymers: Mw vs MFI

**PolyK Technologies, admin@polyktech.com**

specialized in high voltage polymer dielectric and ferroelectric technologies

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<table>
<thead>
<tr>
<th>PVDF Grades</th>
<th>Number average molecular weight $M_n \times 10^3$</th>
<th>Weight average molecular weight $M_w \times 10^3$</th>
<th>Polydispersity index $U_N$</th>
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<tbody>
<tr>
<td><strong>Homopolymers</strong></td>
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<tr>
<td>Solef® 1008</td>
<td>114</td>
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<td>Solef® 1010</td>
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<td>352</td>
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<td><strong>Copolymers</strong></td>
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<tr>
<td>Solef® 11008</td>
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<tr>
<td>Solef® 21508</td>
<td>132</td>
<td>240</td>
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<tr>
<td>Solef® 31508</td>
<td>149</td>
<td>274</td>
<td>1.8</td>
</tr>
</tbody>
</table>

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Note: we do not trust the reported PDI polydispersity index.
1. Both HFP and CTFE are much larger than VDF, so they cannot be crystallized into the crystalline phase of VDF.

2. Therefore higher HFP or CTFE leads to lower crystallinity, and the copolymer can even become totally amorphous if the content of comonomer is higher than 30-40% by wt.

3. Lower crystallinity $\rightarrow$ softer.

4. However, with certain production process, Solvay can produce either “homogeneous” or “heterogeneous” copolymers. The copolymers with heterogeneous chain structure are very unique: the melting temperature does not significantly depend on the comonomer content.
1. Produced by Arkema (Kynar Flex 3120, 2800, and 2500) or Solvay (11008, 21508 and others)

2. Content of HFP:
   • 5-7wt% with Tm > 160 C
   • 10wt% with Tm > 160 C
   • 15wt% with Tm of 140 C
   • 17-18wt% with Tm of 125 C
Content of CTFE, heterogeneous composition:

- 10wt% with Tm > 160 C
- 15wt% with Tm >160 C
- 20wt% with Tm > 160 C
- 32wt% with Tm of 120 C and very soft???
Combine the advantage of PVDF and PTFE:

- We have limited compositions for research and development.
- Tm can be as high as 270 °C but still with dielectric constant >7
Molecular engineering by copolymerization:
• HFP control the mechanical tear resistance.
• VDF increases K and reduces Tm
• TFE reduces K and increases Tm
• We have four compositions and extruded film samples.
Thermoplastic Fluoro-Elastomers

- Rubber-like physical performance but can be processed by solvent cast of extrusion, no curing required.
- Small amount of crystalline phase form physical crosslinking.
- Good materials for electroactive polymer actuators
- $K$ is higher than 5

A, B, C are chemical crosslinking

D is TPE
Chemically Crosslinked Rubber

- Free radical crosslinking
- Or other crosslinking chemical
- Need to avoid air/oxygen during curing

A, B, C are chemical crosslinking, D is TPE
1. Classical ferroelectric polymers as they directly crystallize into the ferroelectric beta phase, stretching is not required.

2. Apply coating and directly poled to piezoelectric performance without stretching.

3. We have eight compositions, two of them with high TrFE content and NON-ferroelectric.

4. Production process: suspension or emulsion.

5. TrFE is explosive and these polymers are very expensive ($5,000/kg)

6. Use as ferroelectric memory in Internet of things (IoT), produced by roll-to-roll printing
P(VDF-TrFE) Copolymers

PolyK Technologies, admin@polyktech.com, specialized in high voltage polymer dielectric and ferroelectric technologies
Lower coercive switching field than PVDF
PVDF-TrFE 80/20 mol

PVDF-TrFE 80/20 film, 132 C Anneal (no stretch)
Second Heating (after melt)

Curie Transition
Operation T up to 120 C

PolyK Technologies, admin@polyktech.com  specialized in high voltage polymer dielectric and ferroelectric technologies
1. Invented by Professor Qiming Zhang at Penn State University in early 2000

2. Achieve high dielectric constant of 50 at room temperature while still have high dielectric breakdown strength,

3. Great materials for high energy density film capacitors, actuators, and electrocaloric cooling devices.

4. Depending on CFE or CTFE contents, still semicrystalline polymers with Tm of 120-140 deg C, and melting enthalpy of 10-25 J/g

5. Produced in small scale for R&D purpose, still expensive >$5,000-$12,000/kg

6. CFE is more expensive than CTFE as CFE is not used by other industry, while CTFE is used in commercial PVDF-CTFE

Relaxor Ferroelectric or Ferrorelaxor Polymers
P(VDF-TrFE-CFE) or P(VDF-TrFE-CTFE)

PolyK Technologies, admin@polyktech.com  specialized in high voltage polymer dielectric and ferroelectric technologies
Relaxor Ferroelectric or Ferrorelaxor Polymer, almost no hysteresis loop, great for actuators

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Specialized in high voltage polymer dielectric and ferroelectric technologies

A broad collection of polar fluoropolymers for R&D


