Perfluoroelastomers are essential engineering materials that can withstand the harshest chemical environments and/or extreme temperatures. These materials have the highest level of chemical and thermal resistance of any elastomer currently available. Perfluorinated elastomers (PFEs) are often used in many industry applications as operating conditions in the oil and gas industry become increasingly severe. Most oil companies expect that future well completions will require the use of aggressive chemistries that hydrocarbon and fluorinated elastomers will be insufficient to withstand. Additional reasons for using PFE include reducing expensive equipment downtime, handling more stringent environmental regulations (e.g., reduced emissions, leak prevention), and/or increasing lifetime performance of the finished article, such as seals (for example, O-rings, V-rings, T-seals and packers) or progressive cavity pumps. Though some minor handling and

Perfluoroelastomers in Hydrocarbon Operations

By Ed Cole, 3M Advanced Materials Division

All factors should be considered thoroughly before selecting a PFE grade.

Above: These offshore oil and gas applications and others use PFE components.
mixing factors for PFE polymers must be considered, typical fluoroelastomer (FKM) and hydrocarbon elastomer mixing and processing equipment are more than adequate to work with PFE materials.

**What Are PFEs?**

Perfluorinated elastomers, often referred to as FFKM (perfluoroelastomers) or PFE, are copolymers of (primarily) tetrafluoroethylene (TFE) and perfluorinated vinyl ether (PFVE). Because of their inherent chemical inertness, they use a cure site monomer (CSM) to enable crosslinking (see Figure 1). These CSMs typically have a free radically reactive bromine and/or iodine atom, or they carry a perfluoroalkyl nitrile group that can be induced to trimerize into a perfluorinated triazine network. Originally developed in the late 1960s, PFE polymers contain approximately 72.5 percent fluorine by weight and do not have any significant hydrocarbon segments in the polymer backbone. The bond dissociation energy of a fluorocarbon bond is approximately 25 to 30 percent higher than a hydrocarbon.

Two primary grades of PFE are offered commercially. The first, a chemical grade, is crosslinked using a suitable peroxide and coagent. The chemical grades are selected for applications in which chemical resistance is the primary concern and temperatures will not likely be excessive. These grades are usually less expensive than other grades and are good for chemical handling and processing, cleaning, and chemical etching processes.

The other major PFE grade is a high temperature (HT) grade, which requires some proprietary catalyst chemistry to form a triazine crosslink network. These materials are selected when performance temperatures exceed 230 C. The perfluorinated triazine networks perform at temperatures continuously up to 315 C with minimal property loss and outstanding compression set resistance.

HT PFE grades are excellent for many thermally extreme processes in which exposure to aggressive chemicals occurs, such as in oil and gas and chemical process industry (CPI) applications.

**Chemical & Thermal Resistance**

For all PFE polymers and cure types, resistance to a variety of chemicals at different concentrations and conditions is exceptional (see Table 1). Chemistries—such as polar solvents that would normally affect other fluoroelastomers negatively—have little to no effect on fully fluorinated elastomers.

The thermal resistance of these materials is also exceptional, even with exposure to otherwise harmful chemistries. For the peroxide/coagent PFE grades, application in temperatures up to approximately 230 C is feasible. The upper temperature range is significantly increased for the HT grades to 315 C because of the exceptional thermal stability of the triazine crosslink.

**Crosslink Chemistries**

A few different crosslink chemistries are used for PFE polymers. Some of the more common include free-radical/coagent cure and catalyst-induced triazine cure. These methods will sufficiently crosslink their respective PFE polymers. However, each has individual benefits and deficiencies. End users should take great care to choose the right cure chemistry and polymer combination for the end-use application. Generally, a post-cure cycle is required to maximize the performance properties of either crosslink system.

The free-radical/coagent cure is most often related to crosslinking chemical PFE grades. Using a bromine or iodine containing cure site

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**Table 1. Generic chemical resistance comparison of fluoropolymers**

<table>
<thead>
<tr>
<th>Base Chemistry</th>
<th>Example</th>
<th>PFE</th>
<th>FKM</th>
<th>TFE/P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aliphatic Hydrocarbon</td>
<td>Propane</td>
<td>++++</td>
<td>++++</td>
<td>++</td>
</tr>
<tr>
<td>Aromatic Hydrocarbon</td>
<td>Benzene</td>
<td>++++</td>
<td>++++</td>
<td>++</td>
</tr>
<tr>
<td>Organic Acid</td>
<td>Acetic Acid</td>
<td>++++</td>
<td>+</td>
<td>+++</td>
</tr>
<tr>
<td>Inorganic Acid</td>
<td>Sulfuric Acid</td>
<td>++++</td>
<td>++++</td>
<td>Varies</td>
</tr>
<tr>
<td>Inorganic Base</td>
<td>Sodium Hydroxide</td>
<td>++++</td>
<td>+</td>
<td>+++</td>
</tr>
<tr>
<td>Ethers</td>
<td>MtBE</td>
<td>++++</td>
<td>+++</td>
<td>+</td>
</tr>
<tr>
<td>Ketones</td>
<td>Acetone</td>
<td>++++</td>
<td>+</td>
<td>++</td>
</tr>
<tr>
<td>Nitrous Oxidizers</td>
<td>Ammonium Nitrate</td>
<td>++++</td>
<td>+++</td>
<td>++++</td>
</tr>
</tbody>
</table>

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**Figure 1. Generic PFE polymer structure with CSM**
monomer (X - CSM; X = Br or I) and a suitable coagent to trap the peroxide-generated free radicals is an excellent choice for application temperatures up to about 230 C and can be used in steam, acid and hot water applications. For crosslinking X-CSM PFE polymers, triallyl isocyanurate’s (TAIC) physical properties and heat resistance provide the best overall performance as a coagent. Because the reaction is peroxide initiated, these materials can become scorchy. Good temperature control during mixing and processing these polymers is vital. Typically, peroxides—such as 2,5-di-methyl-2,5-di(t-butylperoxy)hexane (DBPH)—are used to impede scorching. To form the triazine crosslink network in the HT PFE grades, a proprietary catalyst is used, reacting at a high temperature with nitrile containing cure sites (CN-CSM) to form a triazine ring structure (see Figure 2).

The aromatic heterocyclic structure is very thermally stable with excellent performance up to 315 C (continuous use). Overall chemical resistance is exceptional. However, this crosslink chemistry is susceptible to hydrolysis by steam and/or hot water, rapidly opening the triazine ring and causing the modulus to quickly decrease, which affects sealing and physical performance.

This weakness can be partially overcome by using a dual-cure system with a peroxide/coagent and triazine forming catalyst or using the peroxide/coagent system alone with the CN-CSM containing polymers. Both have advantages and disadvantages.

A dual-cure system significantly improves resistance to hydrolysis and maintains good compression set performance. Using the peroxide/coagent system alone allows for much better performance in steam and hot water with fair-to-good compression set performance. However, using these cure systems with the HT grades reduces upper temperature performance from 315 C to a range of 250 to 260 C.

**Application Considerations**

When considering a PFE material for use in an application, several factors must be considered to ensure that the best polymer and/or cure system is chosen. If the continuous use of a seal will exceed 230 C, a HT PFE grade should be used. Of course, as much as possible, desired physical properties should be known to choose the best grade and curative for the application. For steam and hot water applications, a peroxide/coagent cure alone or with catalyst cure should be chosen.

For applications at temperatures higher than 270 C, a deflection of no more than 20 percent should be used because of the high coefficient of thermal expansion (CTE) of PFE polymers compared to other materials, such as standard FKM. PFE has an average CTE increase of approximately 30 to 40 percent compared to the FKM and hydrogenated nitrile butadiene rubber (HNBR) with the same filler loading and approximately 80 to 90 percent higher than a comparable hardness HNBR. PFE will continue to expand once it reaches maximum temperature and may need about 30 to 45 minutes before reaching a fully expanded equilibrium.

**Markets & Applications**

PFE is gaining a wider acceptance and necessity in the transportation, CPI, and oil and gas markets because of the increasingly demanding application

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R_f = \text{perfluorinated polymer}
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**Figure 2. Triazine ring structure**
environments. The high cost of these materials may be a barrier for many applications. However, PFE is now positioned within many markets in which FKM was 35 years ago. While expensive compared to other materials, it is often chosen because other materials were unsuccessful. Costs associated with the PFE use in desired applications are in line with the expected benefits gained from the efficacy of the final material solution.

Because oil and energy costs are projected to rise, the oil and gas industry is working harder and spending more to achieve economic yields. The days of simply drilling into the ground and oil emerging are gone according to industry professionals. Deeper wells are being drilled, at higher temperatures and in more chemically aggressive environments.

Horizontal drilling requires elaborate engineering feats to extract oil from the ground. Events, such as the Macondo incident in the Gulf of Mexico, have made the reliability of highly engineered components a priority. The need for materials that will perform under extreme conditions is more critical than ever. Applications for PFE in the CPI market are also available. From refining oil into other useful chemistries, to fluid transport, and machinery/material handling equipment, PFE is finding a new home in many areas in which improved chemical resistance is necessary. These applications include:

- Stators/progressing cavity pumps for moving chemicals
- Line stops used for the maintenance of high-temperature and chemically aggressive continuous processes at CPI plants
- Seals/diaphragms for valves and pumps exposed to harsh materials, which extend their lives and increase reliability and safety

The Right Choice

In extreme chemical and thermal conditions across a range of industries, some perfluoroelastomers can be used where other materials fail. Specialized equipment is superfluous for processing PFE polymers.

Simple training and know-how are all that is required. Actual performance is dictated by many factors—including, but not limited to, compound formulation, crosslink chemistry and density, polymer molecular weight, manufacturing conditions, and application conditions. All factors should be weighed carefully before choosing a PFE grade.

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