Long-Term Performance of New, Improved Specialty Fluoroelastomers in Various Aggressive Fluids

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Abstract

More aggressive environments in both automotive and industrial applications as well as a drive for longer part life are increasing the demand for specialty fluoroelastomers. Recent advances in the manufacture of fluoroelastomers have led to the development of several new specialty types of fluoroelastomer that provide significantly improved processing performance. This paper presents data on the long-term performance of these new specialty fluoroelastomers in a number of aggressive fluids, both automotive and industrial, to characterize their performance versus one another. It should also offer some guidance to the part manufacturer on what type of fluoroelastomer to use in their increasingly demanding applications.
### Introduction

Conventional fluoroelastomers (FKM) comprised of vinylidene fluoride (VF₂), hexafluoropropylene (HFP), and optionally tetrafluoroethylene (TFE) have for decades provided excellent service life in both automotive and industrial applications. They are generally crosslinked using a poly-hydroxy cure system comprising a crosslinker such as bisphenol AF and a phase transfer catalyst such as benzyltriphenylphosphonium chloride (BTPPC). While this kind of composition provides an excellent balance of physical properties, fluid resistance and heat resistance, a trend toward more aggressive service environments as well as a need for longer part life is increasing the demand for specialty types of FKM polymer that can provide even higher degrees of chemical resistance than that of the more conventional copolymers of VF₂, HFP and TFE.

### Background

One particular weakness in conventional fluoroelastomers is their susceptibility to attack by strong base. This results in relatively poor resistance to strong caustic solutions and also solutions containing primary and secondary amine additives. Specialty copolymers of TFE and Propylene (P) are known to exhibit excellent resistance to this type of nucleophilic attack, but they also exhibit relatively poor resistance to many hydrocarbon lubricants, particularly when compared to conventional fluoroelastomers. They are also known for relatively poor processability. A new specialty fluoroelastomer that exhibits excellent resistance to base attack, equivalent to TFE/P dipolymers, as well as excellent processing characteristics was recently introduced at the 2002 SAE World Congress ¹.

Other specialty fluoroelastomers that continue to grow in use are the peroxide-cure types. The peroxide-cure system can provide improvements in resistance to certain classes of aggressive chemical and aqueous media. Other examples of specialty fluoroelastomers are those that contain perfluoromethylvinyl ether (PMVE). The incorporation of PMVE results in polymer compositions that exhibit significantly improved low temperature flexibility. While both of these families of polymers bring unique and desirable end use properties, they also have some of the typical disadvantages often associated with the peroxide cure system, i.e. mold fouling, mold sticking and poor hot tear strength. Two papers presented in the Fall 2001 ACS Rubber Division meeting introduced a new generation of peroxide-cured FKM polymers utilizing new technology developed by Dupont Dow Elastomers that greatly improves the processability of these specialty types of polymers²,³.

With the recent introduction of these new specialty fluoroelastomers it was felt it could benefit the part manufacturers to compare them to existing commercial FKM and FEPM polymers in fluids representative of many of the more aggressive types in use today.

### Experimental

In this paper vulcanizates of selected FKM and FEPM polymers have been characterized using standard ASTM test methods. Tests included ASTM D471 immersions as well as compression set testing and various low temperature tests. All polymers evaluated in this paper were compounded using MT (N990) carbon black to provide a nominal 75 durometer Shore A hardness. All compounds were mixed in a standard laboratory Banbury® internal mixer. The experimental polymers studied in this paper were supplied by DuPont Dow Elastomers and are described in Table #1.
Table I

Experimental Polymers

<table>
<thead>
<tr>
<th>Polymer Designation</th>
<th>Monomers</th>
<th>Cure System</th>
</tr>
</thead>
<tbody>
<tr>
<td>VTX-8525</td>
<td>VF₂/TFE/PMVE/ICSM</td>
<td>Peroxide</td>
</tr>
<tr>
<td>VTX-8550</td>
<td>VF₂/TFE/PMVE/ICSM</td>
<td>Peroxide</td>
</tr>
<tr>
<td>VTX-8600</td>
<td>VF₂/HFP/TFE/ICSM</td>
<td>Peroxide</td>
</tr>
<tr>
<td>VTX-8650</td>
<td>VF₂/HFP/TFE/ICSM</td>
<td>Peroxide</td>
</tr>
<tr>
<td>VTX-8802</td>
<td>TFE/P/ICSM</td>
<td>Bisphenol</td>
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</table>

Commercial Polymers

<table>
<thead>
<tr>
<th>Polymer Designation</th>
<th>Monomers</th>
<th>Cure System</th>
</tr>
</thead>
<tbody>
<tr>
<td>FKM A-500</td>
<td>VF₂/HFP</td>
<td>Bisphenol</td>
</tr>
<tr>
<td>FKM B-600</td>
<td>VF₂/HFP/TFE</td>
<td>Bisphenol</td>
</tr>
<tr>
<td>FKM ETP-900</td>
<td>E/TFE/PMVE/CSM</td>
<td>Peroxide</td>
</tr>
<tr>
<td>TFE/P Dipolymer</td>
<td>TFE/P</td>
<td>Peroxide</td>
</tr>
<tr>
<td>TFE/P/VF₂</td>
<td>TFE/P/VF₂</td>
<td>Bisphenol</td>
</tr>
</tbody>
</table>

VF₂ = vinylidene fluoride  
HFP = hexafluoropropylene  
TFE = tetrafluoroethylene  
PMVE = perfluoromethylvinylether  
E = Ethylene  
P = Propylene  
CSM = proprietary cure site monomer  
ICSM = new, improved proprietary cure site monomer

Results and Discussion

Base Resistance

As shown in Figure 1 below, base attack on fluoroelastomers involves the abstraction of HF from the VF₂ monomer, resulting in the formation of sites of unsaturation.

Figure 1

Base Attack on HFP/TFE/VF₂ FKM
The hydrogen that is present on the VF2 monomer, when adjacent to an HFP segment, is relatively acidic and is easily abstracted by a strong base. This extraction leads to the formation of unsaturated sites, which lead to what is essentially formation of excessively high levels of crosslinking in the polymer, resulting in high modulus and low elongation. Too great a loss in elongation can result in a molded part losing its flexibility and in extreme cases becoming brittle. This mechanism is especially problematic in dynamic sealing application where cracks at the sealing surface can cause leakage. Elongation at break as measured per ASTM D412, is a valid measure of a material’s relative ability to resist base attack.

Copolymers of TFE/P, which were developed in the 1970’s, are inherently resistant to base attack because they have no VF2 in the polymer backbone. However, since they are difficult to process they have found limited use. The need for these types of polymers though, has dramatically increased over the years. One such application is in deep drilling where production tooling is exposed to hydrogen sulfide. H2S is highly corrosive, and requires the use of extremely aggressive corrosion inhibitors to protect tooling. Another application is in automotive and heavy-duty powertrains. Automotive lubricant additives have continued to become more aggressive as powerful amine-based corrosion inhibitors and anti-sludge dispersants are being used to extend both the functionality and the service life of oils and greases. A study of the effect of a number of these automotive fluids on different commercial FKM and FEPM polymers was reviewed in a paper at the 2000 SAE World Congress 4. The DuPont Company introduced a TFE/PMVE/Ethylene polymer in the 1980’s, which has begun to replace TFE/P types in some of these applications.

VTX-8802, a new co-polymer of TFE/Propylene exhibits excellent resistance to base attack and has a good balance of physical properties and processing characteristics 1. In figure 2, VTX-8802 is compared to TFE/P, TFE/PMVE/E (ETP-900), as well as the conventional FKM A-500 and FKM B-600 polymers. Testing was conducted for periods out to 1008 hours at 150°C in ASTM Service Fluid 105. This fluid is a particularly discriminating automotive lubricant for evaluating candidate vulcanizates since it is a standard reference fluid that contains an additive package representative of the most aggressive packages used in commercial motor oils.

**Figure 2**

![Percent Retained Elongation](image)

While the standard FKM A-500 and FKM B-600 compounds show large elongation losses in this extremely aggressive motor oil, the VTX-8802 is equal in resistance to both the TFE/P and ETP-900 and virtually unaffected by this oil. Note that this test would have been even more aggressive if the oil had been changed periodically, as is the practice in most automotive engines.
In Figure 3 these same five compounds were evaluated in a very aggressive wheel bearing lubricant package. The additive package used in this lubricant is representative of the most aggressive ones used in current wheel bearing and differential applications. In this test the standard FKM A-500 and FKM B-600 compounds retained less than 25% of their original elongation after aging just 5 weeks at 150°C. The VTX-8802 was again almost unaffected by this lubricant – similar to the TFE/P copolymer and the ETP-900.

Figure 3

Percent Retained Elongation Aged @ 150°C in
Stuarco 7061 Wheel Bearing Lubricant with
6% Stuarco 7098 Additive

In Figure 4 the results of aging in a basic mixture of 30% potassium hydroxide in water for one week at 100°C are shown. In this test the FKM A-500 and the FKM B-600 compound again saw a significant loss in elongation. The VTX-8802, TFE/P and ETP-900 based compounds maintained excellent elongation.

Figure 4

Percent Retained Elongation
Aged 168 Hours @ 100°C
in 30% Potassium Hydroxide in Water

The amount of volume swell in a given lubricant can affect the abrasion and wear resistance in a dynamic sealing application. Therefore, it is also important to look at the relative swell of these compounds in the different lubricants. While the swell of all of these compounds is 5% or less in the wheel bearing lubricant, they swell significantly more in the Service Fluid 105. In this fluid the ETP-900 shows similar swell to a standard FKM, the TFE/P compound swells 14% and the VTX-8802 is halfway in between at 10% swell.
Intermediate Base Resistance

To improve the processability of TFE/P polymers, different levels of VF$_2$ have been added to the polymer to allow curing with a bisphenol-cure system. While these polymers show improvements in base resistance over standard, bisphenol-cured fluoroelastomers, the inclusion of VF$_2$ compromises the base resistance of these polymers. The composition that includes 30% VF$_2$ has found a market in applications that are in contact with fluids that are moderately aggressive. One particular sealing application is dynamic shaft seals used in transmissions, axles and differentials. In these applications it is the balance of base resistance, low temperature properties and processability that has been responsible for their growth. But in most cases the polymer is a compromise in all three areas. It is this 30% VF2 polymer, which is simply listed as TFE/P/VF$_2$ in this paper.

In this section of the paper the intermediate base resistance, TFE/P/VF$_2$ polymer is compared to the two standard FKM A-500 and FKM B-600 based compounds, as well as to four of the new improved processing peroxide-cured polymers and the new base resistant polymer VTX-8802. The four peroxide cured products evaluated are two PMVE-containing products, VTX-8525 and a higher fluorine product VTX-8550, which have glass transition temperatures of $-27^\circ$C and $-25^\circ$C, respectively. They are also compared to two new HFP-containing peroxide cured polymers, VTX-8650 and the higher fluorine VTX-8600. All eight of these polymers are compared in three different automotive lubricants in Figures 6 – 8. In the Petro Canada ATF fluid all but the standard FKM A-500 compound do quite well. After 1008 hours at 150°C, the FKM B-600 still maintained 80% of its original elongation. All four of the peroxide-cured polymers, the bisphenol-cured TFE/P/VF$_2$ polymer and the VTX-8802 saw little to no change in elongation.
Figure 6

Percent Retained Elongation
Aged @ 150°C in Petro Canada Dexron III ATF

In the ASTM Service Fluid 105, which contains a more aggressive additive package, all four of the peroxide cured polymers exhibit better retention of elongation than the TFE/P/VF₂ polymer, which in this case appears to age no better than a standard bisphenol-cured FKM B-600 compound. In this fluid the base resistance of the VTX-8802 is apparent, as it is virtually unaffected.

Figure 7

Percent Retained Elongation
Aged @ 150°C in Service Fluid 105 Oil

In the wheel bearing fluid containing a very aggressive additive package, the standard FKM types and the TFE/P/VF₂ copolymer retain less than 30% of their elongation after aging for 5 weeks at 150°C. In this fluid the peroxide-cured products all retained the same, if not slightly
more elongation than this copolymer. Again, the excellent base resistance of the VTX-8802 is shown.

Figure 8

Percent Retained Elongation Aged @ 150°C in Stuarco 7061 Wheel Bearing Lubricant with 6% Stuarco 7098 Additive

The volume swell after aging 504 hours at 150°C in these same automotive lubricants is shown in figure 9. The peroxide-cured compounds all show the similar low swell typical of a standard FKM compound. The TFE/P/VF₂ polymer and the VTX-8802 are slightly higher in swell exhibiting a swell of 10% and 11% in the ATF fluid and 8% and 10% in the Service Fluid 105 oil.

Figure 9

Volume Swell after aging 504 Hours @ 150°C in Various Automotive Lubricants
Coolant Resistance

The use of specialty types of FKM in aqueous or aqueous blends continues to grow. In automotive and heavy-duty applications, the use of multi-port gaskets can necessitate that the sealing material not just be resistant to oils but also to coolant mixtures. This is coupled with the trend toward long life organic acid (OAT) coolants, which use extremely aggressive amine-based additive packages in water blends. In figure 10 all ten of the FKM and FEPM products are aged out to 1008 hours at 150°C in a 50/50 blend of an extremely aggressive Texaco heavy duty extended life OAT coolant with water. The compounds used in this study were standard quality control compounds and were not specifically compounded for use in an aqueous environment. Both of the standard bisphenol-cured FKM A-500 and FKM B-600 products see significant losses in both tensile and elongation as well as high swell. The bisphenol-cured VTX-8802 and TFE/P/VF₂ polymers do not see these same high losses in physical properties. However, they both show higher swells because of the high level of metal oxides in the formulations. The peroxide-cured products all show significant advantages in this very aggressive environment by exhibiting both good retention of physical properties and also relatively low volume swell. Of particular note is the low volume swell of the two PMVE products VTX-8525 and VTX-8550. This same trend of low swell in aqueous media was noted in Steven’s and Lyon’s ACS papers ²³.

![Figure 10](image_url)

Low Temperature Performance

At low temperatures the modulus of the elastomeric component of a seal increases as the temperature decreases. As the seal becomes stiffer it can no longer exert the sealing force needed to seal or it can lose the flexibility needed to follow a shaft in a dynamic application. Therefore, it is important to match the low temperature performance of the fluoroelastomer to the application requirements. The low temperature properties of all ten of the polymers used in this study are shown in Figure 11.
Vulcanizates based on VTX-8550 and VTX-8525 clearly shows the best low temperature properties. VTX-8650 was slightly better than the two standard FKM polymers with a Tg of –18°C. The TFE/P/VF2 polymer, which exhibited no better base resistance than the VTX-8650, was significantly worse in low temperature with a Tg of –8°C. Of the three base resistant offerings, the VTX-8802 and the TFE/P dipolymer show similar glass transition temperatures of 2°C. The ETP-900 was considerably better at –11°C.

Compression Set Resistance

Standard bisphenol-cured fluoroelastomer compounds are known for their excellent resistance to compression set. The peroxide-cured FKM polymers traditionally have not provided the same high degree of resistance to compression set. In figure 12 the compression set resistance of all ten compounds in this study are measured, including aging periods out to 1008 hours at 150°C. The four peroxide-cured compounds were only postcured 2 hours at 232°C, while the other compounds were postcured a standard 16 hours at 232°C. All four of these peroxide cured compounds showed compression set properties almost equivalent to the bisphenol-cured FKM B-600 compound. Since they all have fluorine contents similar to or higher than the FKM B-600 this is not an unexpected result. This high degree of resistance to compression set was obtained using only a two-hour oven postcure. The effect of postcure on vulcanizates of these new peroxide-cure polymers was discussed in Steven’s and Lyon’s ACS papers. The TFE/P/VF2 polymer had a compression set of 53% after 1008 hours while the VTX-8650 had a compression set of 30%. Also, of particular note, is the excellent compression set properties of the two PMVE containing polymers, VTX-8525 and 8550, with less than 30% set after 1008 hours at 150°C. Of the three base resistant materials, VTX-8802 showed a considerable improvement in compression set properties over the TFE/P or the ETP-900 compounds.
Figure 12

Compression Set Properties in Air @ 150°C

Conclusions

The new polymer VTX-8802 has equivalent long-term base resistance as TFE/P and ETP-900. It has improved resistance to swell in different hydrocarbon based lubricants over TFE/P, however is not as good as ETP-900. The VTX-8802 has improved compression set properties over both the TFE/P copolymer and ETP-900. It has equivalent low temperature properties to TFE/P, but ETP-900 has superior low temperature properties over both of these polymers.

Four new peroxide cured products were evaluated. All four products exhibited better resistance to attack from different amine-based additive packages than conventional bisphenol-cured FKM products. They were equivalent, if not slightly better, than the bisphenol-cured TFE/P/30% VF2 polymer. They all maintained excellent longer term compression resistance with only a short two hour postcure. They all showed an improvement in resistance to new long life OAT coolants over conventional bisphenol-cured FKM products and the TFE/P/VF2 product.

The two PMVE-containing products, VTX-8525 and VTX-8550, showed these improvements as well as excellent low temperature flexibility. The two new HFP-containing peroxide cured products, VTX-8600 and VTX-8650 showed these improvements, plus the VTX-8650 exhibited the same low temperature flexibility of a standard A-type FKM, which was 10°C better than the TFE/P/VF2 product.

All five of these new products will be commercially available by Dupont Dow’s new manufacturing facility in the very near future.
References


