Biofuels Put Seals to the Test

Author: John Kerwin, FInstM, Materials Technology Manager, Precision Polymer Engineering Ltd.

Bio substitutes for conventional oil derived products are becoming increasingly popular. These biomass sources are both renewable and progressively more cost competitive compared with fossil-based oil. However, bio-alternatives can pose processing and storage problems. Although bio sources are often blended with traditional oil-based products to make processing easier, recent research has shown that the increased acidity of the biofuels can have an adverse effect on elastomer seals used in process equipment and storage vessels.

Biofuels are commonly classified into two main categories: ethanol and biodiesel. Ethanol is derived mainly from sugar cane and corn or maize (Bioethanol). It is currently the most significant biofuel with production outstripping biodiesel by ten times. Biodiesel, on the other hand, is derived from a variety of sources. These include oils from rapeseed, sunflower, palm, and soya and animal fats mainly produced in Europe, which is also its major market.

Both these biofuels are used commercially as blends with conventional oil based gasoline and diesel, with ratios of 90% gasoline/10% bioethanol being most common. Diesel blends are conventionally 5% biodiesel blends with 95% conventional oil based diesel but ASTM (American Society for Testing and Materials) specifications are now in place for a range of blends up to 20% biodiesel.

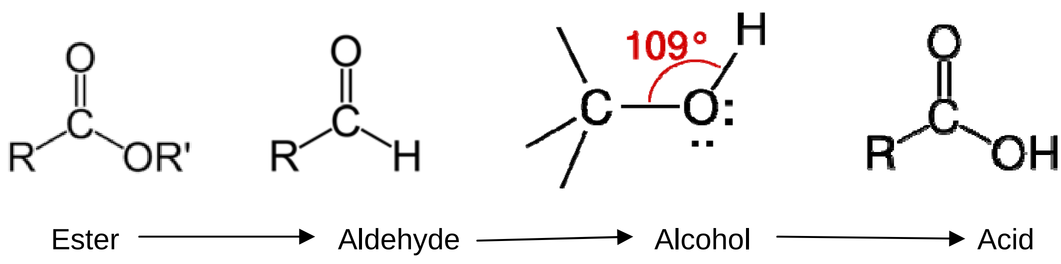
Elastomer Swelling

An elastomer or rubber is a polymer with the property of elasticity. It is typically made up of carbon, hydrogen, oxygen and/or silicon atoms. Chemical or fluid absorption by an elastomer can lead to swelling of the seal. It is prone to attack by fluids exhibiting the same polarity, a phenomenon described as 'like-dissolves-like'. For example, ethylene-propylene rubber (EPDM) is a 'non-polar' elastomer, and as such, should not be used to seal non-polar solvents such as hexane. However, EPDM can be used to seal against polar fluids such as water.

For many conventional gasoline and diesel applications, NBR (nitrile butadiene rubbers) are widely used. There are a variety of grades available which, depending upon their acrylonitrile content, will have varying degrees of fuel and high temperature resistance. Increasingly, in hot under bonnet applications, FKM (fluorocarbon) rubbers are now being used due to their greater temperature resistance. However both these material types run a significant risk of swelling when exposed to biofuels and biofuel blends.

In the case of Biofuels, the chemical nature of the fuel blends is significantly different from that of oil based gasoline or diesel. Ethanol is a polar solvent and not compatible with many of the elastomer grades that are used with non-polar gasoline. The higher the blend ratio of ethanol the more significant the effect will be, leading to excessive swelling and a deterioration of sealing properties over time.

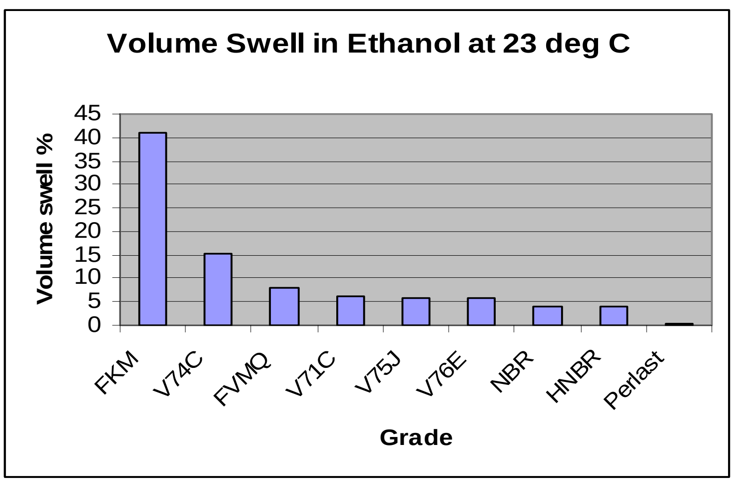
With Biodiesel the chemical compatibility situation is more complicated. The originating chemical structure generated from the biomass is that of a methyl ester. Over time and the inevitable exposure to atmospheric oxygen, biodiesel undergoes chemical changes as described below, producing carboxylic acids and lowering the fuel's pH.



Test results over 12 months

Long terms immersion testing of various elastomers over 12 months has been conducted to assess the effects of biofuel and biodiesel fuel chemistries on elastomers typically used with traditional gasoline and diesel.

Effect of Ethanol



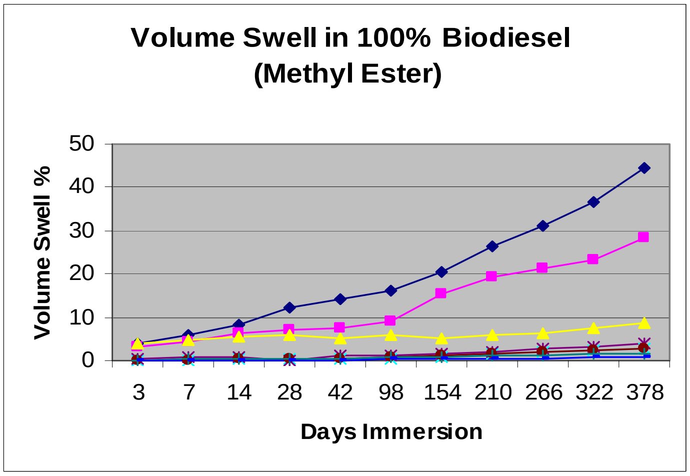
The graph shows the effect of ethanol on a fluoroelastomer - one of the most popular types of elastomer for gasoline. Interestingly the other grades are FKMs as well, but their chemistry is different. This highlights an important fact that fluorocarbon materials experience varying degrees of chemical attack, dependent upon how the base polymer is blended with other ingredients in order to produce a finished moulding material, and the method of curing.

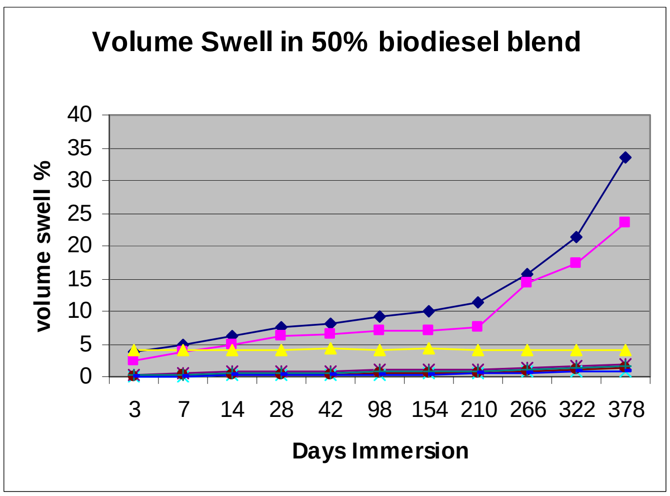
Within the fluoropolymer (FKM) family of materials, there are differing 'cure systems' – the chemical cross-linking reaction (vulcanization) which occurs to join the polymer chains together. Common FKM materials are the well known 'A' and 'B' grades. The backbone of 'A' and 'B' grades are made up from hexafluoropropylene (HFP), vinylidene difluoride (VF_2) and (for the 'B' types) tetrafluoroethylene (TFE). 'A'-type fluoroelastomers are mostly cured by utilizing a 'condensation' reaction where water is generated during the cure process. Biodiesel can reverse this FKM cure mechanism, breaking down the cross-links of the material, and leading to premature failure.

On the other hand a peroxide-cured fluoroelastomers is a ‘free-radical’ reaction, and as such, does not undergo a reversible reaction. This is the curing system used in Elastomers **X-Y** and should be used with biofuels.

Interestingly NBR performs well in both gasoline and ethanol which suggests it could be used for both fuels as long as the temperature remains below 120°C. Above this hydrogenated NBR (HNBR) can be used up to 180°C and peroxide-cured FKM above this.

Effect of Biodiesel





Legend : A = Conventional NBR
B = Conventional HNBR
C = Conventional FVMQ
D = Biofuel FKM grades
(*Will add letters to charts*)

These tests indicate that NBR and HNBR are severely affected by biodiesel, based on the 'like dissolves like' polarity of the rubber and biodiesel, and should be replaced with a peroxide cured

FKM which shows little swelling over the 12 months immersion.

Also observed in the biodiesel test was the increasing acidity of the fuel, caused by oxidation, over the 12 months. Moreover, water contamination of the biodiesel will accelerate the hydrolysis of fatty acid methyl ester to carboxylic acids, further increasing the acidity. In both these cases the increased acidity will accelerate the rate of elastomer swelling.

In conclusion...

The 12 month ethanol and biodiesel immersion tests have shown that:

Conventional NBR elastomers can be used within their normal operating parameters for both conventional gasoline and gasoline / ethanol blends. However they suffer from significant swelling with biodiesel.

Bisphenol-cured FKM elastomers should be replaced with peroxide-cured FKM for biofuel and biodiesel applications.

The rate of swelling varies depending on the immersion conditions, for example aged fatty acid methyl ester is more aggressive than fresh fatty acid methyl ester.

The move to biofuels has been rapid so the challenges and implications for seals and their effectiveness are not yet fully understood by many involved in its manufacture, handling, processing and delivery. The immersion tests reported here give an insight into the kinds of sealing issues faced by companies processing and handling biofuels. For more in-depth guidance on the most suitable sealing solutions for specific biofuel applications contact John Kerwin at Precision Polymer Engineering on +44 (0)1254 295400 and e-mail: john.kerwin@prepol.com.