

B20 to B100 Blends as Heating Fuels

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The following is an excerpt from *B20 to B100 Blends as Heating Fuels*, released November 2018

Pump Seal Material Evaluation

Oil burners commonly used in homes and smaller commercial applications are fixed firing rate, with pressure atomized burner nozzles. Fuel pressure delivered to the nozzle is typically 100 – 150 psi. The fuel pump in these systems are gear-type positive displacement pumps which include the following features:

- An integral pressure regulator with adjustable discharge pressure.
- Some type of flow control which only allows flow to the nozzle when the pump is running and quickly turns the flow on and off during cycling operation.
- An inlet strainer.
- High suction lift to rapidly clear air out of an empty suction line.

In oil burner pumps there are several different seals used. In consultation with the pump manufacturers and other industry stakeholders, the pump shaft seals were identified at the start of this project at the area of most concern. A leaking shaft seal has potential to allow oil to drip onto the floor of the home, an undesirable outcome.

The most common pump types used in North America include lip-type shaft seals with a specific nitrile material. Less common, but still important are carbon-face type shaft seals. In this section of this report, work done on the basis interaction between the nitrile used in most pump shaft seals and biodiesel blends is presented. The evaluation of pumps under operating conditions with lip seals and carbon-face seals is discussed in the next section.

The work that is the subject of this section has been focused on the impact that biodiesel blend use can have on the nitrile seal material used in the market-dominant fuel pump shaft seal. This is a nitrile lip seal and, while the focus is on this specific seal, nitrile generally is used in other legacy heating system seal applications including other pump, filter, and valve components. The focus on this specific seal was a decision made in consultation with pump manufacturers. A leak in the shaft seal could potentially lead to fuel spillage inside of the building space.

Figure 1 provides a photo and sketch of the lip seal used in the burner pump installed in a strong majority of building heating applications in the U.S. It is a common double-lip type seal with a

metal casing. The seal is pressed into to pump body during manufacture and is not practically field-replaceable.

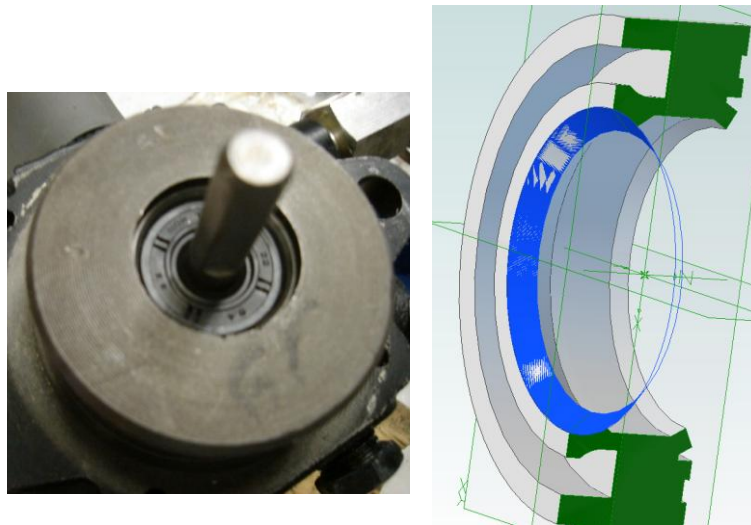


Figure 0-1 Typical oil burner fuel pump shaft seal

In legacy heating systems, the dominant seal material is nitrile-acrylonitrile butadiene rubber or NBR; an unsaturated copolymer constructed of acrylonitrile and butadiene monomers. The presence of the acrylonitrile monomer imparts permeation resistance characteristics to a wide variety of solvents and chemicals, while the butadiene component in the polymer contributes toward the flexibility.

Like any given polymer, the mechanical properties of nitrile vary depending on its constituents. Differences in composition may be based on the acrylonitrile content used in synthesis (commercial nitrile rubber can vary from 25% to 50%), reinforcement fillers, plasticizers, antioxidants, processing aids, and cross-linking agents [2, 3].

In the process of obtaining a listing approval for a burner for application in this market, testing is typically done, guided by Standard UL 296 [4] which effectively incorporates material compatibility tests for elastomeric materials, UL 157 [5]. This test involves an immersion period of 70 hours at 23 ± 2 °C (73 ± 3.6 °F). Suitable elastomers are required to retain more than 60% of their unconditioned tensile strength and elongation and volume swell must fall within the range of -1 to +25%.

Generally, nitrile materials have good resistance to petroleum products and are commonly used with heating oil applications. The chemical resistance, however, of nitrile to biodiesel fuel or biodiesel/heating oil blends was not as well established. There are nitrile materials offered commercially which are at least nominally compatible with biodiesel blends to the B-100 level [6].

In a study published in 1997 [7, 8] Southwest Research Institute reported on their evaluation of a range of different elastomer types exposed to biodiesel/petroleum blends. Fuels included in this study included JP-8, B-100, low-sulfur diesel fuel, “reference” diesel fuel and blends at the B-20 and B-30 level. Samples were immersed at 51.7 °C (125 °F) for 0, 22, 70, for 694 hours. Tests reported in the study by Southwest Research Institute showed a notable effect of the biodiesel blend on the nitrile materials. This included volume swell in the 20% range and a reduction in tensile strength as high as 38%. These tests were done prior to the implementation of oxidation reserve specifications and the lowering of the acid value specification for B100, and at higher temperature and for much longer times than required by UL 157. Even so, the magnitude of property change reported is within the acceptable range under UL 157, although marginally.

In a more recent study [9] Southwest Research Institute and the National Renewable Energy Laboratory, evaluated the compatibility of several elastomers including three different types of nitrile in B20 blends and ethanol-diesel blends. The nitrile materials included a general purpose NBR, and high aceto-nitrile content rubber, and a peroxide-cured nitrile rubber. These materials were selected as being typical of materials used in automotive applications. Samples were immersed at 40 °C (104 °F) for 500 hours.

Tests reported in the earlier study by Southwest Research Institute for elastomers common to diesel engines showed some effect of the biodiesel blend on the nitrile materials. This included volume swell in the 20% range and a reduction in tensile strength as high as 38%. The later study reported on by SwRI and NREL showed no significant effect of the biodiesel blends on the NBR materials studied, leading to the conclusion “all of these elastomers appear to be fully compatible with 20% biodiesel blends”.

In another, potentially relevant study done by Underwriters Laboratories [10] the compatibility of B5 blends with elastomers typically used in oil burner applications was studied in compliance with the UL157 standard. Two specific nitrile materials were included. This study showed no significant effect of the biodiesel blend on the materials tested.

The goal of the work done in this project was to extend the prior NBR elastomer studies on biodiesel compatibility to the entire range from B0 to B100 and to focus specifically on the NBR material used in legacy pump shaft seals in oil burner pumps. This specific component was selected cooperatively with equipment manufacturers as potentially the most vulnerable part of existing systems. A key question for this study was the “limit value” i.e. the maximum amount of biodiesel that could be used in a legacy system at least based on this one specific metric.

The experimental work reported in this section was done by Dr. Chad Korach and Richard Anger at the State University of New York at Stony Brook under contract to BNL, as part of this project.

Experimental

In this study the impact of biodiesel at a wide range of blend levels was evaluated for the nitrile material commonly used on legacy oil burner pumps in the U.S. Sheets of the nitrile material

were obtained with assistance from the Suntec Corporation. The specific material is grade A795 NBR from the NOK corporation [11]. Samples of this material were cut into standard dog bone shapes as well as circles and rectangular shapes. Immersion with different biodiesel / No. 2 oil blends was done for 670 hours at 51.7 °C (125 °F).

After immersion, all samples were removed from the oil, cleaned, and then subjected to non-destructive hardness and swell measurement tests prior to the destructive tensile or compression set tests. The cleaning process consisted of a ~3 second acetone dip to remove residual oil, and blotting with laboratory tissues to dry. All samples, both discs and dog bone specimens, were used to measure the volume swell and hardness; dog bone samples only were used to measure tensile strength; and the disc samples only were used to measure the compression set of the materials.

The biodiesel fuel used in this effort was a commercial sample, received from Hero BX, Erie Pa. The No. 2 fuel oil used was also a commercial sample, obtained locally.

When biodiesel degrades during extended storage, one possible eventual outcome is the formation of organic acids. The current ASTM standard which defines biodiesel as a blend stock, provides a limit of TAN, or total acid number of 0.5 maximum, down from initial industry specifications of 1.2 and the first ASTM D6751 specification of 0.8. To evaluate the potential impact which severely degraded fuel might have on the target elastomer, some tests were done in which biodiesel samples with high acid numbers were used. These high acid numbers were achieved by adding decanoic acid to the fuel samples to achieve TAN levels far higher than the allowed limit. All of these elevated acid number tests were done using just biodiesel (B100). Decanoic acid was selected for use in this study because it is highly soluble in biodiesel and fuel oil and it was the organic acid used to produce biodiesel at the limit of acidity in the UL study of B5 blends [10].

Hardness

Samples were tested per the ASTM D2240 Durometer Hardness test. A Type M durometer (Checkline RX-1600-M attached to a Checkline OS-3 test frame, Figure 1) was used which lowers a hardened steel pin into contact with the sample, measuring deformation and determining Durometer (M) rating on a scale of 0 to 100. The instrument was calibrated using Type M standard materials prior to each set of samples tested. For each specimen 10 durometer measurements were made and then averaged for a group of specimens. Measurements were made at the center of the dog bone sample base, and the disc sample centers. Durometer hardness is reported as a function of conditioning protocol.



Figure 0-2. Type M Durometer used for hardness measurements of the nitrile samples before and after exposure to fuels.

Volume Swell

Samples were measured for volume swell per ASTM 471 Fluid Aging test. All specimens, dogbone and discs, were weighed both in air and while submerged in water, using a specimen sling, before and after oil immersion. Specimens were dipped in acetone and blotted with lint free lab paper prior to measurements to remove residual surface water or oil. Archimedes principle is used to calculate the percent change in volume from the mass values, as the body's density (and volume) are related to the buoyancy forces acting on the samples while submerged in water. The % volume change (ΔV) is computed by the equation:

$$\Delta V = \frac{(M_3 - M_4) - (M_1 - M_2)}{(M_1 - M_2)}$$

Where, M_1 is the initial mass of the sample in air, M_2 is the initial mass of the sample in water, M_3 is the mass of the sample in air after oil immersion, and M_4 is the mass of the sample in water after oil immersion.

Tensile Strength

Tensile strength of the nitrile was tested per ASTM D412 Tension test. Sample geometry of the nitrile samples were die-cuts (ASTM D638 Type V) from a ~2 mm nitrile slab using a hardened steel die in the shape of dog bone specimens with initial gauge cross-section width of 3.175 mm and thickness of ~2 mm. Samples were tested using a screw-driven uniaxial load frame (TiraTest 26005, Figure 2) fitted with pneumatic-actuated grips and a 0.5 kN load cell. After the cleaning process, samples were immediately gripped in an un-stressed position and load was applied using a crosshead rate of 500 mm/min as per ASTM D412. A computer-controlled data acquisition system was used to control the experiment and to record the load and displacement data simultaneously at a 50 Hz sampling rate. Testing was completed after sample rupture which resulted in an immediate loss of load. Tensile strength (S_t) is computed from the force at failure and the nominal cross-section prior to loading by the equation:

$$S_t = \frac{F_f}{A_o}$$

Where, F_f is the applied on the specimen at failure, and A_o is the initial cross-sectional area, computed by the width and thickness of the gauge region for each specimen.

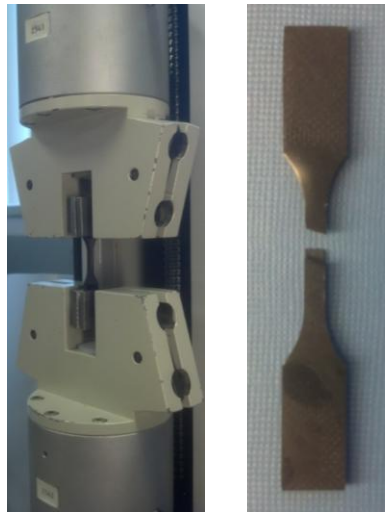


Figure 0-3 Tensile testing to failure of nitrile samples performed with a TiraTest 26005 uniaxial load frame with pneumatic grips (left); Nitrile dogbone specimen after testing to failure (right).

Compression Set

Samples were tested for resistance to permanent compressive deformation per ASTM D395 Method B, Rubber Property Compression Set Under Constant Deflection in Air. Nitrile disc specimens were compressed ~20% (varying by individual specimen's post-exposure thickness) in a polished steel, chrome plated compression rig (Figure 1-4) separated by calibrated, hardened steel spacer shims. Bolts were used to apply the compressive load to the platens. Once the samples were engaged in the compression rig the entire rig was placed in a 51.7°C (125°F) furnace (Blue M) for 22 hours. Sample thickness was measured before and after compression set testing to compute changes in relaxed height and to determine the percent of plastic deformation to original compressive deformation (Compression Set) C_B by:

$$C_B = \frac{(t_o - t_i)}{(t_o - t_n)} \cdot 100$$

Where t_o is the original sample thickness after the oil immersion conditions, but prior to compression set testing, t_i is the final sample thickness after the compression set conditions, and t_n is the spacer thickness.

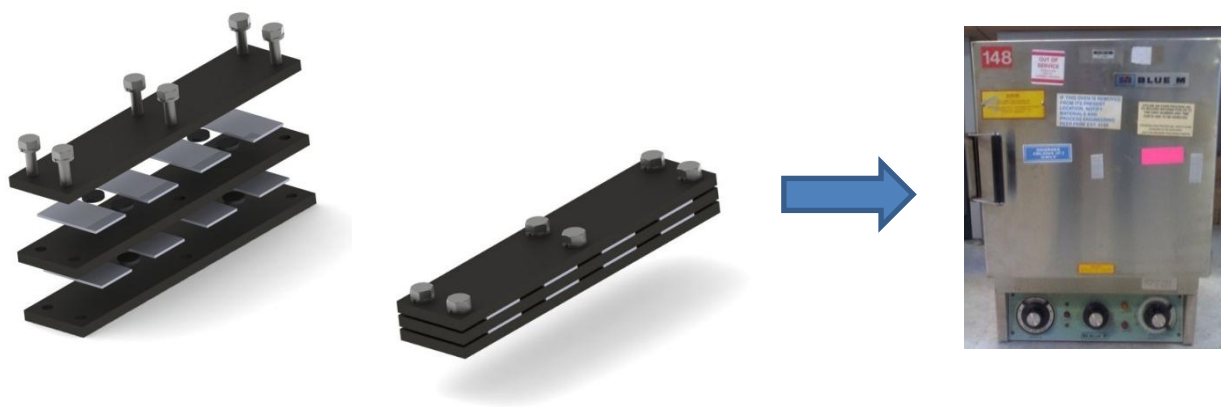


Figure 0-4 Compression set of nitrile samples induced with chrome-plated pressure plates per ASTM D395 to 20% strain (left and center). Specimen thickness change was measured after 22 hours at 125°F in a laboratory furnace (right).

Results

Figure 1-5 to 1-8 present the results of testing done with different biodiesel blend levels. Figure 1-5 shows the tensile strength results. Averages of three area measurements were used for each specimen. Results of tensile strength are reported as a function of the oil immersion protocol and do not illustrate a clear trend with biodiesel level. In all cases the elastomer easily retained greater than 60% of the unexposed tensile strength.

Figure 1-6 shows the results for the hardness measurements. There is a slight trend toward greater hardness retention with increasing biodiesel level in the blend but these results also show no concern about biodiesel interaction. Figure 1-7 shows results for compression set but again the impact is very small. Figure 1-8 shows the volume swell. There is no clear trend with increasing biodiesel content and all values are clearly less than the nominally allowed 25% under UL 157.

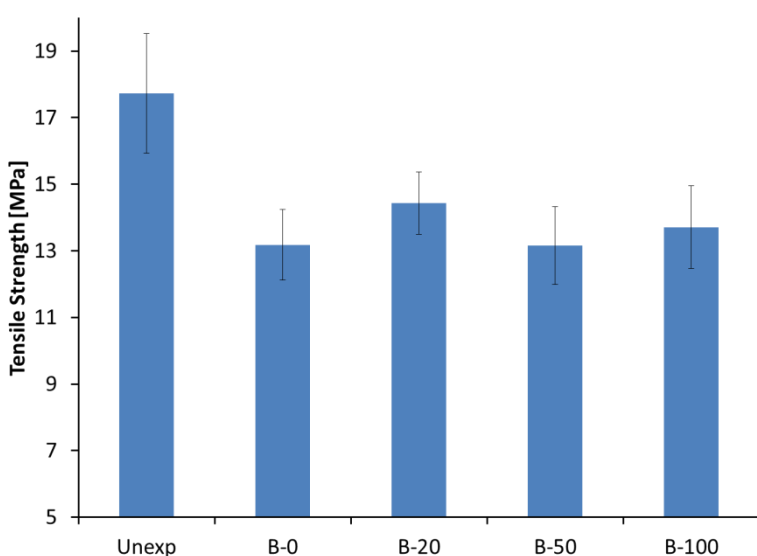


Figure 0-5 Impact of biodiesel content on measured tensile strength

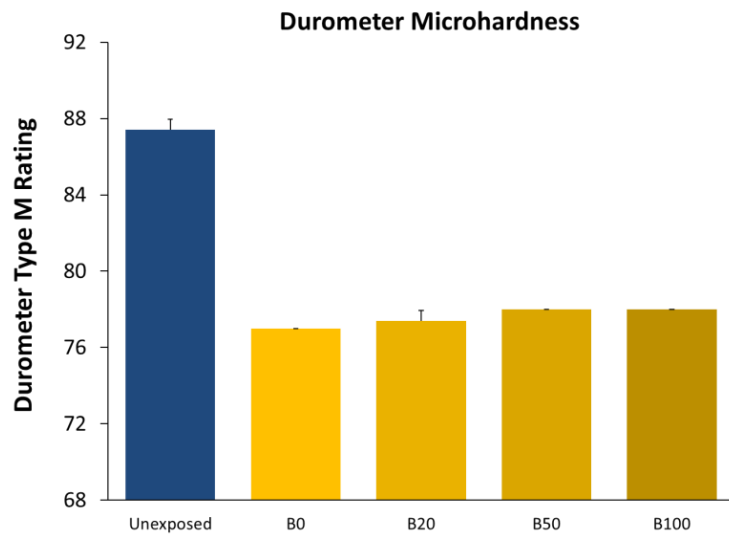


Figure 0-6 Impact of biodiesel content on measured hardness

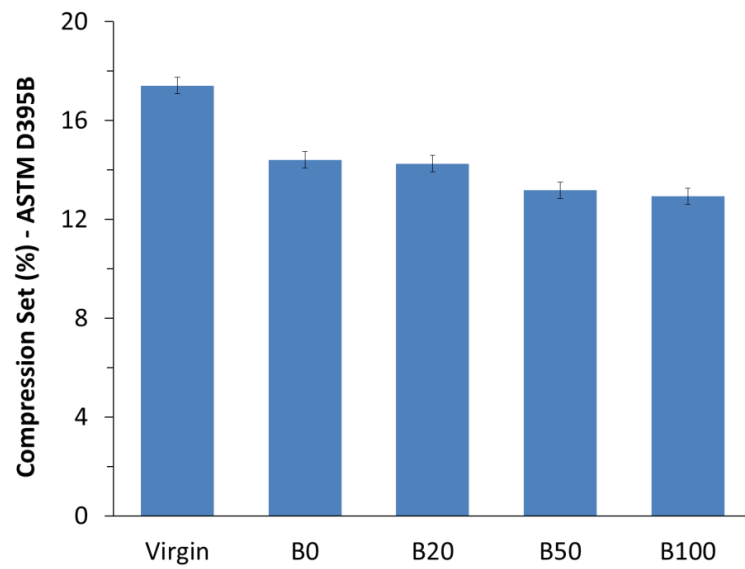


Figure 0-7 Impact of biodiesel content on measured compression set

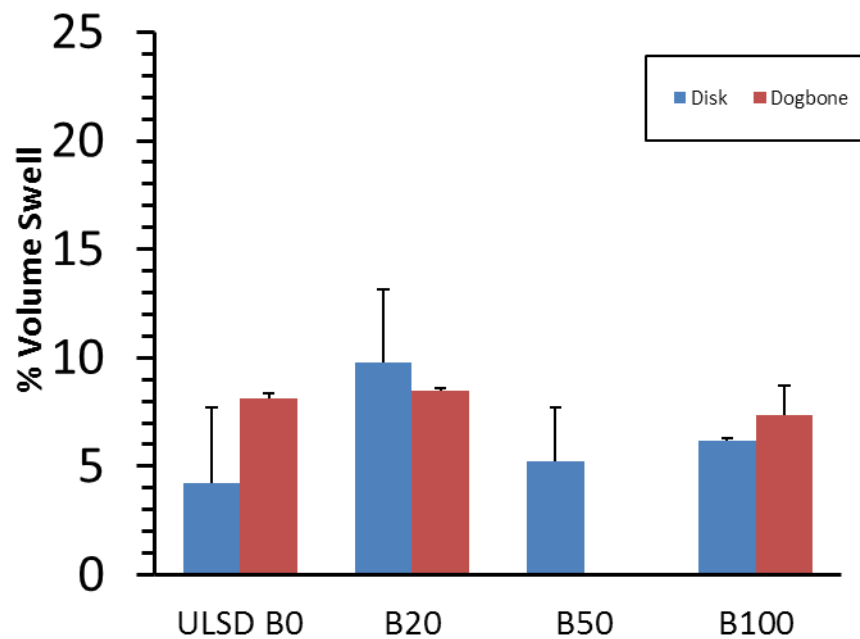


Figure 0-8 Impact of biodiesel content on measured volume swell

Figures 1-9 through 1-12 present the results of the studies with B-100 with elevated acid number. Figure 1-9 shows the impact of elevated acid number on tensile strength. Using the criterion in UL 157, a tensile strength of less than 10.5 MPa would be under the 60% of the unexposed sample tensile strength. Samples exposed in biodiesel with a TAN of 2 or greater would not be considered an acceptable outcome.

As shown in Figure 1-10, the impact of acid number on hardness is not very significant and a trend is not apparent. Figure 1-11 shows a clear increase in compression set with increasing acid number. UL 157 does not set a limit on either of these parameters, however.

Figure 1-12, volume swell shows a strong increase in this parameter with acid number. At an acid number of 2 the limit of 25% swell in UL 157 has been reached.

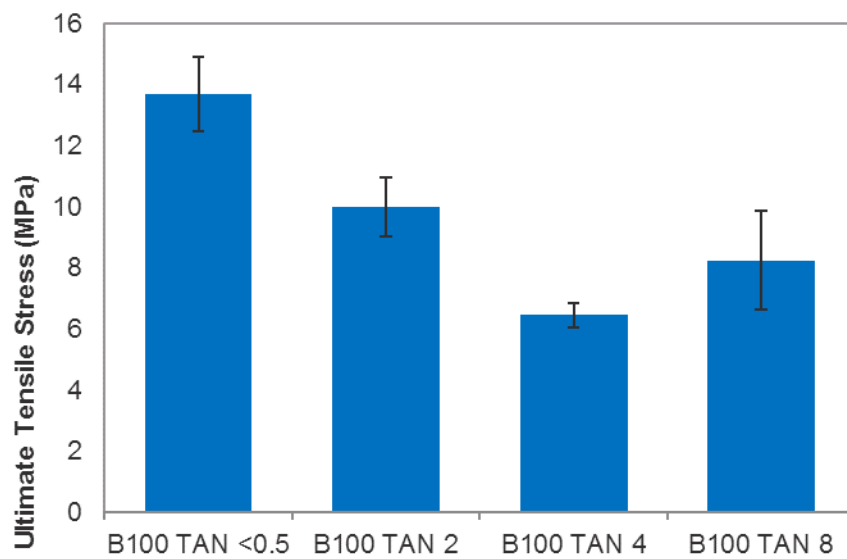


Figure 0-9 Impact of elevated acid number on tensile strength. B-100.

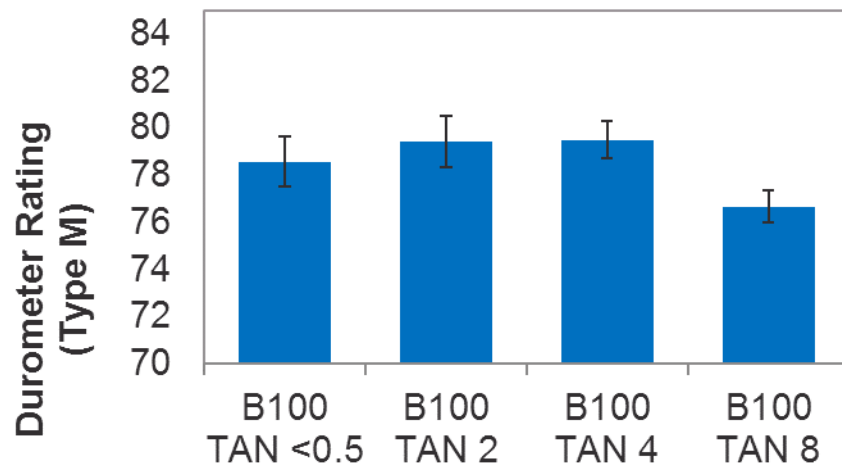


Figure 0-10 Impact of elevated acid number on hardness

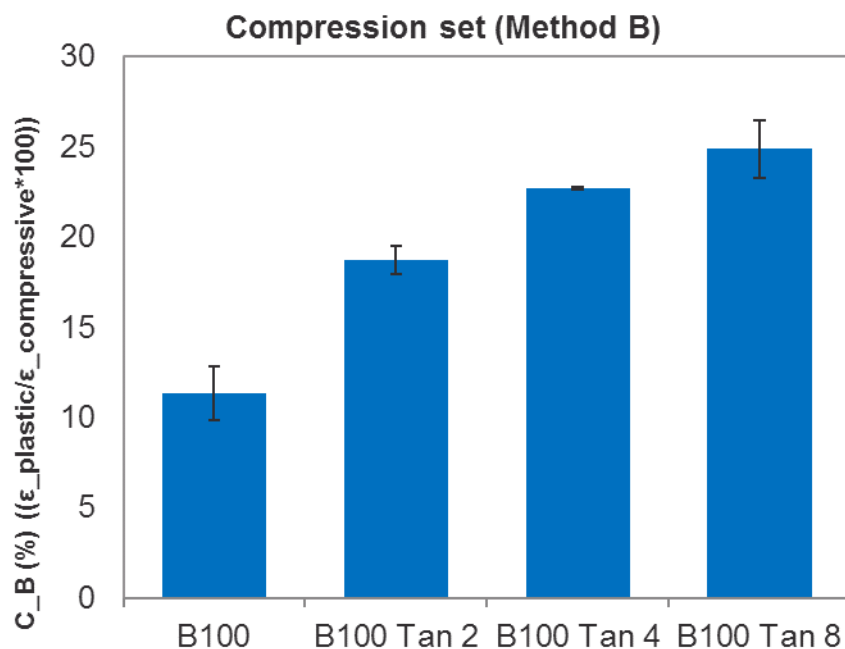


Figure 0-11 Impact of elevated acid number on compression set.

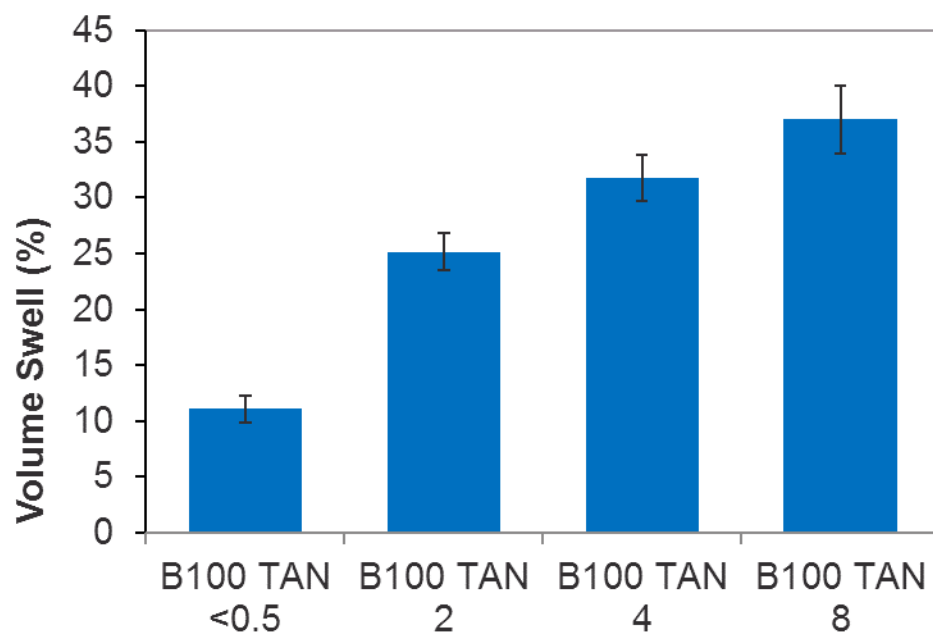


Figure 0-12 Impact of elevated acid number on swell

Discussion

Conventional elastomer impact testing under the UL 157 procedure is by soaking the fuel for a total of 70 hours at room temperature (~73°F). For this testing, much higher temperatures (125°F) and much longer soak times (670 hours) were used. For biodiesel/heating oil blends

meeting current ASTM standards the results presented above show no significant changes in the properties measured with biodiesel blend levels to 100% for the specific elastomer evaluated relative to the base fuel oil. This elastomer, which is used in current and legacy oil burner pump shaft seals, was selected as a critically important seal component representative of elastomers generally used in oil-fired heating systems. The results with biodiesel/heating oil blends meeting today's ASTM standards, do not provide a cause for concern about biodiesel use in these systems.

With the elevated acid number, using the decanoic acid, there is, however, a very clear interaction between the fuel and the elastomer when acid numbers are well in excess of the current limits in ASTM D6751 and this has important implications for two reasons. First, if a biodiesel fuel is produced with high acid number or if a biodiesel fuel degrades during extended storage to yield such an extremely high acid number, there could be concerns about elastomer behavior. Such high acid numbers are unlikely to occur in practice. Second, many of the prior studies which have been done on elastomer – biodiesel (i.e. methyl esters of oils and fats) interaction were prior to the implementation of oxidative reserve limits and lower acid value limits for biodiesel. In some of these studies the TAN of the fuel used is not reported. This approach could lead to inaccurate conclusions from previous studies about elastomer suitability with biodiesel meeting today's ASTM standards.

Conclusions

This work has focused specifically on the nitrile elastomer used in the shaft lip seal on the home heating burner pump used in most oil-heated homes in North America. With biodiesel that is not degraded, i.e. has an acid number which meets the current specification for biodiesel blend stock for both acid value and oxidative reserve which serve to minimize the likelihood for acid formation during use, no significant impact of the biodiesel on the elastomer was observed at blend levels to B100. This is based on time periods and temperatures which could be considered conservative relative to those used in practice for material qualification.

When the acid number of the biodiesel blend was elevated through the addition of decanoic acid, significant impact on the elastomer was observed. While today's ASTM specification have been designed to prevent such degradation, severely degraded biodiesel with acid numbers above 2 could lead to accelerated degradation of seal materials.

References

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