

# Plastic Materials for Fuel-Handling Applications

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Plastic resins are used throughout the petroleum-supply chain, in oil & gas exploration, production, refineries, distribution, and ultimately in automobiles. Some examples of applications are in flexible pipes and umbilicals for offshore exploration (Figures 1 & 2), pipe for natural gas distribution, underground pipes for gas stations,<sup>1</sup> holding tanks, tower packing, piping and pumps in the refinery process, and fuel lines in trucks and automobiles. Plastics are a valuable alternative to metals that can be subject to corrosion, especially with more aggressive fuels. Just as in selection of appropriate metallurgy, it is important to select the right plastic material for each application. This article compares three families of broadly used plastic materials: polyethylene, polyamides, and polyvinylidene fluoride (PVDF).

When selecting plastics, engineers must consider both the ability to

meet the initial requirements and how, under those conditions, the material changes over time. Plastics do not corrode like metals, but used under the wrong conditions, they can be subject to swelling, loss of mechanical properties, and decreased temperature resistance. Our study evaluated the change in key properties of plastics materials in a range of fuels. Fuels containing from 10% ethanol to 85% ethanol and biodiesel were used to evaluate plastics materials at temperatures of 40°C and 60°C for up to 6 months of exposure. Mechanical testing was done to show the ability of the plastics to maintain their properties over time. Permeation testing was done to show the plastics' abilities to contain the fuels and protect the environment over time. Previous studies have shown that there is little change in the glass transition temperature or storage modulus when PVDF is exposed to fuels at a range of temperatures.<sup>2</sup> This study

shows that PVDF has the broadest range of potential applications for the oil & gas industry and gives recommendations on the use of each of the families of plastic materials.

## Experimental Methods

### Materials

The materials, fuels, temperatures, and test intervals used for the study were carefully selected. The fuels C, CE10a, and 20% biodiesel were selected because they are currently in use by the general population, while CE85a was chosen for its aggressive nature and potential use in the future. The aggressive versions of these fuels were chosen to represent the worst-case scenarios for the study. Aggressive fuels contain peroxides and copper ions that help initiate the degradation of the polymers. The PVDF grades in this study were selected because they were the most widely used grades for fuel applications or their behavior in fuels



Figures 1 & 2. Offshore umbilical utilizing Kynar® PVDF, polyethylene, or Rilsan® polyamide 11. Used in oil exploration platforms.



required investigation. Kynar® 740 will be referred to as PVDF, Kynar Flex® 2850 will be referred to as PVDF Flex 2850, Kynar Flex® 2800 will be referred to as PVDF Flex 2800. The nylon 12 grade was selected because it is currently used for fuel-line applications. The HDPE grade in this study is used for fuel-pipe applications by one of Arkema's customers.

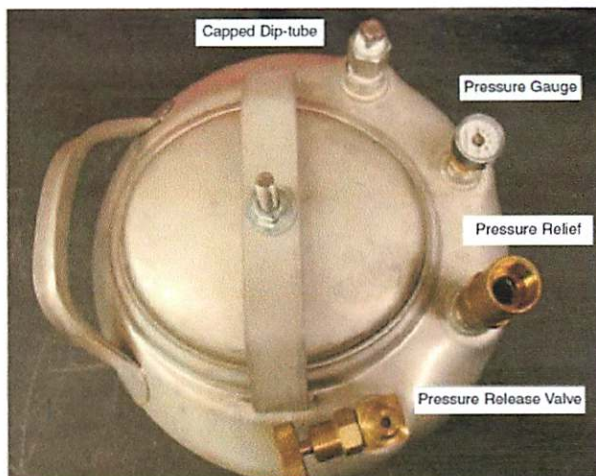
The compositions of the fuels used in the studies are as follows:

- Fuel C: 50% toluene / 50% iso-octane
- CE 85a: 7.5% toluene / 7.5% iso-octane / 85% ethanol
- CE 10a: 45% toluene / 45% iso-octane / 10% ethanol
- B20: 20% biodiesel / 80% diesel

### **Immersion procedure**

The 40°C temperature was selected to closely match the UL971 specification of room temperature and 38°C. The 60°C temperature was highest temperature that could be safely used without risk of reaching the flash point of the fuels. Additionally, 40°C and 60°C are commonly used temperatures in permeation testing, and it was important to keep these temperatures consistent throughout the entire study. Test intervals were selected based on the expected trend of the data. Large changes were expected to occur at the beginning of the exposure, with little change as the exposure time increased past six weeks. More data needed to be collected in these early stages of testing before the materials became saturated with the fuels. The testing was performed for 6 months to allow the materials to fully saturate with fuel and for the data curves to plateau. Data were collected at 3 days, 1 week, 2 weeks, 6 weeks, 3 months, and 6 months.

To safely expose the test specimens to fuel at elevated temperatures, we used one-gallon stainless-steel pressure vessels with a pressure rating of 142 psig at 38°C. The pressure vessels were outfitted with additional fittings. Pressure gauges were installed



**Figure 3. Pressure vessel for immersion samples.**

to monitor the interior pressure, ensuring the safety of the workers. A pressure-relief valve rated for 75 psig was installed as a precautionary measure to prevent the internal pressure from reaching the critical pressure of the vessel. Special seals were used to ensure that there were no leaks. Gas chromatography was performed on fuel from multiple vessels during the exposure to ensure that the fuel composition was not changing.

Specially designed explosion-proof ovens were used for the study. The chambers had no heating elements. A high-velocity airflow system was used to move through a prescribed pattern to generate heat. All wiring was completely enclosed in specially designed enclosures. Data loggers monitored and recorded oven temperatures every 4 hours during the entire study. This data was downloaded and reviewed regularly to ensure the accuracy and safety of oven temperatures.

### **Tensile and elongation properties**

ASTM D 638 Type I tensile specimens were injection molded for each material. Specimens from each material were exposed at each temperature in each fuel at each time interval. Two separate Instron devices, tabletop models 4201 and 4202 with the 5500R retrofit and long travel extensometer, were used to perform the testing per ASTM method D 638.

Round-robin testing was performed during the study to ensure that data were consistent between both machines. ASTM method D 638, which specifies a 2-inch per minute strain rate, was used. A long travel extensometer collected strain data and had a gauge length set to 2 inches. The Instron's grip separation was 3.75 inches. Special

care was given to the consistency of the testing procedure. All samples were kept in fuel until just before testing. Specimens were then removed from the fuel jar, tapped dry with a tissue, and tested immediately.

### **Weight and length gain**

ASTM D 638 Type I tensile specimens, 40 specimens per fuel at all three temperatures, were cut and stamped with labels. Each specimen was cut to a specified length with two flat ends for reliable measurements and then measured for weight and length. To ensure repeatable measurement, each end sample was cut square and the samples were put into the calipers at the same spot in the same direction for every measurement. An electronic caliper with 0.01-mm accuracy was used to measure the lengths of the specimens. The caliper interfaced with a PC and the measurements were recorded directly into an Excel based spreadsheet. Weight-gain measurements were performed using an electronic scale with 0.1-mg accuracy. The scale was interfaced with a PC and the measurements were recorded directly into an Excel-based spreadsheet. We collected data at exposures of 3 days, 1 week, 2 weeks, 6 weeks, 3 months, and 6 months.

### **Permeation**

Permeation tests were performed using thin-walled (0.015 inch)



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Figure 4. Permeation vessel.



Figure 5. Permeation vessels in oven tray.

3/8-inch OD tubing that was 300 mm long. The permeation vessels that were designed for this study were set up differently from those we traditionally used (Figure 4).

The vessels were placed into the ovens at a slight angle with the tube at the lower end to ensure that the entire vapor region was in the vessel (Figure 5).

The free end of the assembly allowed for expansion of the tube. This setup also allowed for leak testing of the vessels before they were filled with fuel. The assembled vessel was pressurized with 20 psig of nitrogen and submerged in water. If the vessel had a leak, the nitrogen would form bubbles and float to the top, alerting the operator to the problem. Vessels were filled with various fuels and exposed to temperatures of 40°C and 60°C. To improve the reliability, tests on each fuel/material/temperature combination were performed in triplicate. Vessels were removed from the oven periodically and weighed using an electronic mass comparator with 0.1-mg readability and a maximum capacity of 2500 grams. During the weighing process, the atmospheric

pressure, temperature, humidity, and dew point were recorded. These values were recorded to allow for buoyancy correction of the permeation vessels. At each weighing session, a blank vessel was also measured and blank corrections were performed. Permeation rate as defined by Fick's Law is Permeation Constant (g-mm/m<sup>2</sup>day) x Area/Thickness x Pressure. Since pressure is assumed to be the vapor pressure of the fuel and constant throughout the testing, pressure is neglected. This leaves only the permeation constant, the area, and the thickness.

According to the Society of Automotive Engineers (SAE), during gravimetric testing, the permeation constant is defined as a set of eight weight-loss data points in a period of time that when fitted with a straight line have less than 5% error from the

first point to the last, or in statistical notation, a linear regression or R<sup>2</sup> value between 0.95 and 1. We continued our study until this condition was reached for each vessel.

In this study the error was reduced from 5% to less than 0.3%. This was done with many advances in the testing procedure. Two of the main factors were the use of a mass comparator with the 0.1-mg readability and the introduction of the blank correction.

### Material Property Testing

#### Permeation testing

Permeation is an important property inasmuch as polymers are used as barriers in multilayer systems. These systems could be polymers protecting metals or polymers protecting other polymers and ultimately the environment. For example, Kynar Flex is used as the barrier layer for underground fuel piping. These multilayer structures can have both economic and performance benefits, while protecting the soil. The barrier layer not only needs to be resistant to the fuels, it must also protect the other layers from fuel exposure.

In Table 1, the permeation at 40°C is quite varied depending on the polymer/fuel combination. PVDF and PVDF Flex permeation was very low across the range of fuels. Nylon had problems with high permeation in alcohol-containing fuels. HDPE permeation was generally higher across the range, with especially high rates for Fuel C and CE 10a.

Table 1. Permeation of Fuels at 40°C (g/m<sup>2</sup>day).

Material	CE 85a	Fuel C	CE 10a	B20
PVDF	0.94	0.22	1.8	0
PVDF Flex 2850	1.3	0.4	2.2	0
PVDF Flex 2800	2.25	1.06	4.1	0
HDPE	12.81	208.03	206.72	14.27
Nylon 12	259.31	19.71	19.29	0



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Figure 6. Multilayer underground fuel pipe with Kynar Flex® PVDF as inner contact layer. Photo courtesy of OPW Fuel Systems.

## Weight Change

When immersed at 40°C for 6 months, all grades of PVDF and PVDF Flex resins had less than 3% weight change in all fuels. Nylon had high weight gain in the alcohol-containing fuels, as expected, at over 5%. HDPE had higher levels of weight gain for the whole range of fuels, except CE 85a, where nylon had the highest levels. Figure 7 shows these results. This is consistent with the change in tensile properties described in the following section when the

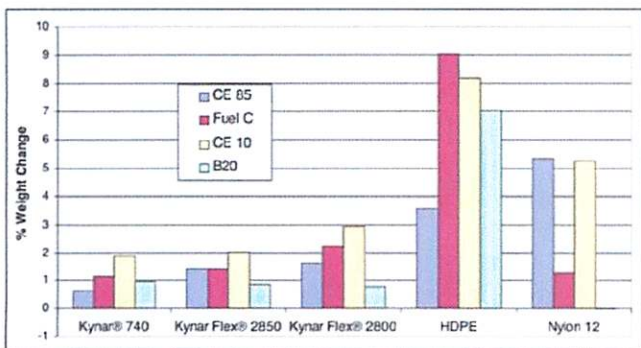


Figure 7. Percent weight change @ 40°C.

Table 2. Tensile Strength Testing @ 40°C.

Material	CE 85a (% Change)	Fuel C (% Change)	CE10a (% Change)	B20 (% Change)
PVDF	-0.61	10.72	-2.21	15.49
PVDF Flex 2850	-1.42	4.39	-4.62	14.22
PVDF Flex 2800	-0.79	8.03	-8.96	17.92
HDPE	-3.03	-2.91	-13.19	-4.91
Nylon 12	-21.71	6.78	-19.79	16.17

other mechanisms are considered. PVDF and PVDF Flex tensile and weight gain are minimal as they relate to the fuel, while HDPE's weight gain and tensile loss are fairly high. For nylon 12 in alcohol-containing fuels, the removal of the plasticizer and increased absorption of alcohol result in a net increase in tensile properties. The removal of the plasticizer dominates the properties, in this case resulting in a brittle product over time. In non-alcohol-containing fuels like biodiesel, nylon 12 sees a net higher rate of tensile change and lower weight gain with lesser removal of the plasticizer and increased tensile due to recrystallization effects.

## Tensile strength

Table 2 shows the tensile strength of the tested plastics immersed at 40°C for 6 months. The PVDF and PVDF Flex resins showed the smallest negative changes in tensile strength during

exposure to CE 85a and CE10a.

Some increase in tensile strength was seen in Fuel C and B20 for PVDF and PVDF Flex resins, due to the known phenomenon of recrystallization<sup>3,4</sup> that takes place at elevated temperatures between  $T_g$  and  $T_m$ . Table 2 also shows that the alcohol-containing fuels are clearly an issue for nylon 12, with higher alcohol-containing fuels lowering the tensile strength. The opposite effect is seen with nylon in Fuel C and B20 as the combination of recrystallization, absorption of fuel, and the removal of the plasticizer make the nylon more rigid. HDPE maintained its tensile strength fairly well in all fuels except CE10a.

Figure 8 shows the effect of increased temperature on tensile strength. All materials were immersed at 40°C and 60°C for 6 months. As the temperature was increased to 60°C, PVDF and



Figure 8. Tensile strength change in biodiesel with changes in temperature.



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PVDF Flex resins showed lower increases in tensile strength as the absorption increased slightly with the higher temperature. HDPE absorption increased with higher temperatures, resulting in lower tensile strength. With nylon, the removal of plasticizer and recrystallization increase the tensile strength at the higher temperature. Only PVDF (Kynar 740) and PVDF Flex 2850 (Kynar Flex 2850) resins were within 10% of their original strength values.

It should also be noted that biodiesel can be soy methyl ester (SME)-based and is not stabilized. SME biodiesel has the potential for high peroxide content, which can lead to secondary oxidation products like alcohols, acids, and aldehydes, making the fuel more aggressive. These oxidation products have a larger effect on materials like HDPE and nylon, which don't have as broad a range of chemical resistance as PVDF and PVDF Flex resins.

### Conclusions

- PVDF and PVDF Flex resins exhibit low permeation levels to most fuels while having low weight gain.
- PVDF and PVDF Flex have out-

standing retention of physical properties in fuel service and, compared with other materials, can provide extended service life.


- PVDF and PVDF Flex resins are highly effective for use over a wide range of fuels. Nylon's physical properties deteriorate and permeation levels become high with high levels of ethanol in the fuel. The opposite is true of HDPE, where performance deteriorates with higher toluene and iso-octane concentrations.

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