

## Compatibility Assessment of Plastic Infrastructure Materials with Off-Highway Diesel and a Diesel Blend Containing 20 Percent Fast Pyrolysis Bio-Oil

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### ABSTRACT

The compatibility of plastic materials used in fuel storage and dispensing applications was determined for an off-highway diesel fuel and a blend containing 20% bio-oil (Bio20) derived from a fast pyrolysis process. Bio20 is not to be confused with B20, which is a diesel blend containing 20% biodiesel. The feedstock, processing, and chemistry of biodiesel are markedly different from bio-oil.

Plastic materials included those identified for use as seals, coatings, piping and fiberglass resins, but many are also used in vehicle fueling systems. The plastic specimens were exposed to the two fuel types for 16 weeks at 60°C. After measuring the wetted volume and hardness, the specimens were dried for 65 hours at 60°C and then remeasured to determine extent of property change. A solubility analysis was performed to better understand the performance of plastic materials in fuel blends composed of bio-oil and diesel.

All of the plastic materials evaluated in this study exhibited higher solubility (volume swell) with the Bio20 fuel blend. This result was predicted by the solubility analysis. However, there were two notable exceptions; the volume swell results for high density polyethylene (HDPE) and polypropylene (PP) did not correlate with their respective solubility curves. HDPE and PP were also unique in that they were the only two plastics that exhibited pronounced volume expansion in the baseline diesel test fuel.

The plastic materials which showed the best compatibility to the bio-oil blend were the barrier plastics polypropylene sulfide (PPS), polyethylene terephthalate (PET or Mylar™), and polytetrafluoroethylene (PTFE or Teflon™). Polyvinylidene fluoride (PVDF or Kynar™) is also used extensively as a permeation barrier material; however, it swelled over 15% when exposed to Bio20. Four grades of nylon were evaluated and the petroleum-derived nylons (Nylon 6, Nylon 6,6, and Nylon 12) showed good compatibility with the test fuels. In contrast, Nylon 11, which is derived from vegetable oil, expanded over 4% with Bio20. HDPE also swelled around 4%, but did so with both test fuels. Two acetal materials and polybutylene terephthalate (PBT) were also observed to swell to 4% with Bio20. Four fiberglass resins were included in the study and they exhibited 10-18% volume expansion. High volume swell was also noted for PP, the PET polyethylene - glycol copolymer (PETG), and polythiourea (PTU). PP also expanded over 15% following exposure to the baseline diesel test fuel.

**CITATION:** Kass, M., Janke, C., Connatser, R., Lewis, S. et al., "Compatibility Assessment of Plastic Infrastructure Materials with Off-Highway Diesel and a Diesel Blend Containing 20 Percent Fast Pyrolysis Bio-Oil," *SAE Int. J. Fuels Lubr.* 8(1):2015, doi:10.4271/2015-01-0893.

### INTRODUCTION

Renewable fuels are becoming more widely used as a transportation fuels in the United States and in other countries. A key motivation for increasing biofuel use is to reduce petroleum consumption, thereby improving energy security and independence [1]. Oil, derived from biomass, is being evaluated as one means of offsetting foreign petroleum imports as well as utilizing a renewable energy source to meet the energy demands in the United States. Most efforts have focused on utilizing bio-oil in burners as a replacement for off-highway diesel (used in home heating applications) or in power generation. However, some efforts are considering bio-oil as possible drop-in additive to diesel fuel.

One popular means of producing bio-oil is through fast pyrolysis of biomass [2, 3, 4, 5, 6] as a substitute for crude petroleum or diesel fuel. Bio-oil differs from both biodiesel and green diesel fuels in that it does not involve conversion of vegetable oils. Biodiesel is derived via transesterification and is primarily composed of fatty acid methyl esters. Green diesel (sometimes referred to as renewable diesel) is produced by hydrocracking or hydrogenation of vegetable oil. In contrast, bio-oil is typically made via pyrolysis of hardwood tree pulp and the specific tree species does affect the resulting chemistry of the fuel. As a result, the composition of these oils varies widely, but they usually contain significant quantities of oxygenates, ketones, and phenols.

The fast pyrolysis method to produce bio-oil employs rapidly heating biomass feedstock (typically pelletized wood) at rates up to 1000°C/s (or higher) in the absence of oxygen. Liquid yields can be as high as 75% depending on the reactor configuration and process. The oil produced in this process has high viscosity and water content (relative to diesel fuel) as show in [Table 1](#) [2].

[Table 1. List of selected properties for pyrolysis oil and diesel](#) [2].

Property	Pyrolysis Oil	Diesel
Density at 20°C, g/cc	1.2	0.85
Viscosity at 20°C, cStoke	13	2.5
Lower heating value, MJ/kg	17.5	42.9
Ash, wt. %	0.13	<0.01
Water content, wt. %	20.5	0.1
Oxygen, wt/%	42.5	0.9

At this stage the bio-oil is immiscible with petroleum-based fuels. Additional upgrading, including hydrotreating and deoxygenation, are necessary for bio-oil to be used with conventional transport fuels such as diesel, kerosene, and gasoline [3]. Much of the oxygen exists as furanics, phenolics, and carboxylic acids, such as acetic and formic acids. These acids are difficult to remove and are corrosive to many infrastructure metals [3, 4, 5, 6, 7, 8, 9, 10].

In 2012, the U. S. Department of Energy Bioenergy Technologies Office initiated a research program to evaluate the compatibility of bio-oil with infrastructure materials. These materials include metals, which are subject to potential oxidation corrosion, and polymers. Like metals, polymer degradation can occur via direct chemical reaction, but unlike metals, polymer performance is also highly affected by its mutual solubility with contacting fluid. Many infrastructure polymers, whether elastomer or plastic, are in fact chemically unreactive to carboxylic acids, petroleum transport fuels, and bio-derived fuels. However, pyrolysis oils contain appreciable levels of phenols, ketones, and aromatics, and these compounds are highly soluble to some plastics. In fact, ketonization of existing carboxylic acids is gaining interest as an additional upgrading step to mitigate metal corrosion in bio-oil [10]. Unfortunately ketones are known solvents for many polymers. The implication is that many existing plastic materials used in fueling infrastructure and vehicle fuel delivery systems may not be compatible with bio-oils and their blends with diesel fuel or other heavy-grade fuel types.

Because plastic materials are commonly used in both rigid and flexible piping and fuel storage systems, volume expansion will impart stress on a rigidly-held plastic component. These internal stresses will reduce the durability of the part and may lead to cracking. Excessive swelling will result in buckling or leakage. Plastics used as permeation barriers need to exhibit low solubility to prevent contamination of less durable plastic materials typically used as wall structures. Failure of a structural plastic may lead to fuel leakage, which subsequently, may create a fire, explosion, or an environmental hazard. As such, it is necessary to understand the performance of plastic materials when they are exposed to new fuel chemistries, such as fast pyrolysis oils, in order to provide guidance on material selection, and identification of potential leak sites and conditions in fueling hardware.

In 2013 ORNL initiated a study to evaluate the compatibility of fueling infrastructure materials to test fuels representing off-highway diesel fuel (which is also used as home heating oil) and Bio20. Another objective was to perform a solubility analysis for each material type and bio-oil blended diesel fuel. The materials included in this study were those used as permeation barriers, flexible piping reinforcement and outer walls, fiberglass resins, coatings and other common plastics. It is important to note that many of these materials are also used in vehicle fueling systems.

## SOLUBILITY AND ITS IMPACT ON OTHER PLASTIC MATERIALS

For polymers, fuel compatibility is predominantly determined by the mutual solubility between a polymer and fuel. In practice, the degree, or extent, of solubility, is routinely assessed by measuring the volume expansion of the polymer being considered. In lieu of direct measurement, the solubility potential between a polymer and solvent can be gauged by calculating the difference in the solubility parameters between the two components using the Flory-Huggins solution theory [11].

Solvents and solutes (or, in this case, fuel and plastics) having similar solubility parameters will have a higher affinity for permeation and dissolution than those with dissimilar values. There are several different solubility approaches. The Hildebrand method is one dimensional and uses a single parameter to represent the total attractive force. In contrast, the more precise (3D) Hansen method utilizes three separate parameters based on atomic dispersion, polarity, and hydrogen bonding. For the purposes of facilitating discussion, the total solubility parameter is often used since it is a single representative parameter. The total solubility parameter is square root of the sum of the squares of the three Hansen parameters. It roughly approximates the Hildebrand parameter and the two are often confused with each other.

The total solubility parameters for mixtures of gasoline blended with ethanol and diesel blended with bio-oil are shown in [Figure 1](#) as a simplified means of displaying this effect. In this figure, the x-axis presents both ethanol-blended gasoline and bio-oil-blended diesel fuel. As shown, the total solubility of gasoline and diesel increases linearly with ethanol and bio-oil respectively. Also depicted in the figure is the typical range of solubility parameters for many plastics (and elastomers). The chart shows that gasoline containing 10 to 50% ethanol is within the shaded polymer solubility range. In contrast diesel fuel containing 0 to 90% bio-oil is within this same range. The implication is that diesel blended with bio-oil can be expected to be soluble to many polymers irrespective of bio-oil content. High solubility translates to high levels of polymer swelling, which is not desirable in many plastic applications since it can lead to buckling and damage.

Another consideration is that many polymer materials are complex compositions of one or more polymers, including low molecular weight (LMW) additives, such as oligomers, plasticizers, stabilizers,

lubricants, or other flexing agents. The extent to which these additives are solvated and extracted by fuel blends also can be assessed using solubility analysis.

The compatibility of a polymeric material typically refers to the solubility of the polymer to a particular solvent. It can also mean susceptibility to chemical attack, although the majority of the polymers and test fuels evaluated in this study were not considered to be chemically reactive with each other. Solubility is typically assessed by measuring the volume swell of the polymer exposed to the solvent of interest. Swell is almost always accompanied by a decrease in hardness (softening) that also affects performance.

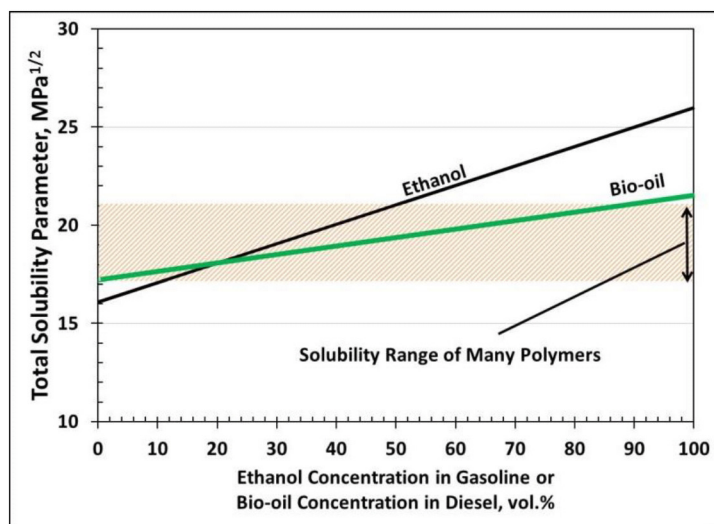


Figure 1. Total solubility parameter curves for gasoline blended with ethanol and diesel fuel blended with bio-oil.

## MATERIALS, EQUIPMENT AND PROCEDURE

### Test Fuels

In this study the baseline fuel was off-highway diesel fuel (also referred commercially as heating oil, #2, dyed, combustible, NA1993 Diesel Fuel 3) which is also designated at home heating oil. The baseline fuel was supplied by Connell Oil, Inc. and had a sulfur concentration up to 500ppm. It is important to note that this particular fuel is the same as that used to fuel off-highway vehicles.

The bio-oil used in this study was produced by a proprietary fast-pyrolysis method and partially upgraded to remove carboxylic acids. The oil was also hydrotreated to remove most of the water component, but it likely that some water remained afterwards (even though the bio-oil was fully miscible with the baseline diesel fuel). The chemical composition of the bio-oil was examined using gas chromatography mass spectrometry (GC-MS) analysis. The analysis showed the presence of significant levels of phenols, ketones, ethyl acetate, and the aromatics (toluene and naphthalene). This composition is similar to other bio-oils derived from fast-pyrolysis, except that acetic acid normally present in bio-oil was esterified to

ethyl acetate. Most bio-oils produced via fast pyrolysis contain levels of acetic ranging from 5 to 10%. The Bio20 test fuel was prepared by splash blending.

### Description of Plastic Materials

Plastic materials are divided into two classes: thermoplastics and thermosets (or thermosetting resins). Thermoplastic polymers do not undergo a chemical change in composition when heated, though they do soften or melt. When cooled they typically return to their original composition, and consequently, they can be molded repeatedly.

Thermosets, on the other hand, can only be cured and shaped once. After forming, they remain in a highly rigid state and cannot be melted. In the thermosetting process, the chemical reaction forming the cross-linked polymer is not reversible. A complete listing of the plastic materials according to type and application is shown in Table 2. For each material type, three specimens were exposed in the test fuel liquids. Each specimen measured 2.54 cm (1 in.) wide, 7.6 cm (3 in.) long, and 0.32 cm (0.125 in.) thick.

Table 2. List of plastic materials and their respective applications.

Thermoplastics	
Application	Material type
Permeation barrier	Polyphenylene sulfide (PPS)
	polyethylene terephthalate (PET)
	polyvinylidene fluoride (PVDF)
	polytetrafluoroethylene (PTFE)
Flexible piping wall material	Nylon 11, Nylon 6, Nylon 6,6 and Nylon 12
	High density polyethylene (HDPE)
Other common plastics	Acetals: Polyoxymethylene (POM) and POM co-polymer
	Polyesters: Polybutylene Terephthalate (PBT), PETG (PET co-polymer)
	Polypropylene (PP)
	Polythiourea (PTU)
Thermosets	
Application	Material type
Fiber reinforced plastic piping and storage tanks	Isophthalic polyester resin (2 types) Terephthalic polyester resin Novolac vinyl ester resin

### Thermoplastics

Thermoplastics are usually pliable, and as a result, they are used in the construction of flexible piping systems. The more chemically resistant grades are also used as high performance seals. The thermoplastic materials examined in this study are grouped according to their application and type as shown in Table 2. The first group includes those used as permeation barriers and liners in flexible piping systems. This group includes polyphenylene sulfide (PPS), polyethylene terephthalate (PET), polyvinylidene fluoride (PVDF), and polytetrafluoroethylene (PTFE). PTFE (also known as Teflon) is also used in sealing applications. PET (or Mylar) is the most commonly used barrier plastic, primarily because it has a lower cost relative to the other three materials.

The second grouping includes nylon and HDPE, which are also used in flexible piping systems. These materials typically do not have the permeation resistance (or high cost) of the four barrier materials, but they do exhibit good compatibility and are used to reinforce and support flexible piping, either as braided fiber bundles or as high strength secondary wall materials. Four grades of nylon were included. Nylons 6 and 6,6 are similar to each other and have good mechanical properties. Nylons 12 and 11 are also used in flexible piping. It is worth noting that Nylon 11 is manufactured from vegetable oil, while the other three are derived from petroleum.

The third grouping includes those plastics which are widely utilized across a range of applications. Acetals (POM and POM copolymer) are used in automotive fueling systems and PTU is a common fuel system component coating material [12]. Other common materials include polybutylene terephthalate (PBT), polyethylene terephthalate co-polymer (PETG), and polypropylene (PP).

### Thermosets

Unlike thermoplastics, thermosets can only be cured and shaped once. After forming, they remain in a solid (highly rigid) state and cannot be melted. Heating will result in oxidation and thermal breakdown rather than softening. In the thermosetting process, the chemical reaction forming the cross-linked polymer is not reversible. Thermosets are used in rigid applications, especially as resins in fiber-reinforced plastics (FRPs), and as adhesives to bond flanges and pipe sections. FRPs are used extensively in fuel storage applications and rigid piping systems.

The thermosets examined in this study included two types of polyester resins (isophthalic and terephthalic polyesters). These resins represent legacy and current resins used in the construction of underground storage tanks and FRP systems. The two types of isophthalic resins differed according to the ratio of isophthalic acid to maleic anhydride. One formulation has a 1:1 ratio of isophthalic acid to maleic anhydride and is representative of resins used in FRP systems (including underground storage tanks) prior to 1990. The other isophthalic polyester resin has a 1:2 ratio of isophthalic acid to maleic anhydride, and was introduced during the 1990s. The terephthalic acid polyester resin has a 1:1 ratio of terephthalic acid to maleic anhydride and was also introduced in the 1990s for use in FRP systems. A vinyl ester resin material was also included which is representative of a newer high-performance formulation used in the construction of FRP systems.

It is important to note that the thermoset specimens consisted of pure resin only. In actuality, these resins are never used without some level of fiber reinforcement, which serves to constrain expansion and increase fracture resistance, strength, and durability. Therefore, the performance of pure resins to the test fuels does not necessarily correspond directly to the actual reinforced samples. However, should the resin become degraded, the composite itself will be less durable. It is also important to note that in addition to being used as the matrix material in FRP, these resins may also be used as adhesives to connect piping and flanges.

### Experimental Protocol

Sealed stainless steel vessels having an interior volume of 175 liters were used to expose the specimens to the test fuels. The specimens were attached to mounting brackets, which were affixed to the inside surface of a cylindrical liner placed within each vessel. To achieve dynamic flow, each chamber was equipped with a paddle to impart a rotating fluid flow at a rate of 0.8 m/s past the specimens. These chambers were sealed to prevent fuel leakage and employed a heating jacket to maintain a constant temperature of 60°C during the exposure period. Each container was filled to a predetermined level with each test fuel. The majority of the specimens were completely submerged in the test fuel liquid, while a second set of specimens were positioned above the liquid fuel line in the headspace for exposure to the vapor-phase environment. The vapor exposure results are not included in this paper.

A flow chart highlighting the treatments and measurements for each material type is shown in Figure 2. The specimens were exposed to the test fuels for a period of 16 weeks, then they were removed and measured for volume, mass, and Shore D hardness while in the wetted (or saturated) state. The volume change for each specimen by the measuring the mass increase (or decrease) using the protocol described in ASTM D543-06 [13]. The hardness measurements were performed according to ASTM D2240 [14] at five locations for each specimen. Once the wetted properties were measured, the elastomers were heated in an oven at 60°C for 65 hours (in air). Afterwards, each specimen was once again measured for volume, mass, and hardness. The changes in these properties from the baseline (untreated) condition were used to assess compatibility.

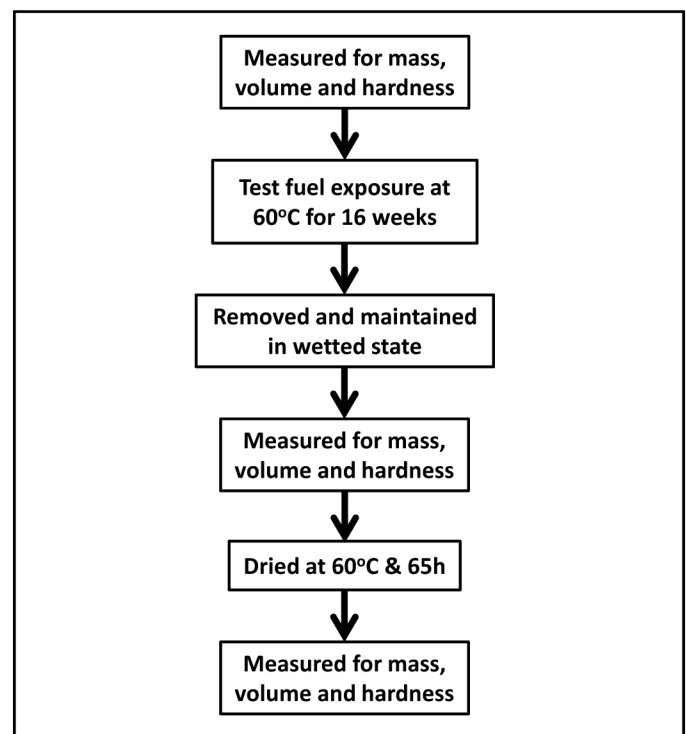


Figure 2. Flow chart showing the exposure protocol and test methods.

## RESULTS

### Chemical Analysis of Bio-Oil and Derivation of Solubility Parameters

The bio-oil sample used in this study was partially upgraded to remove water normally present following pyrolysis. It was found to be completely miscible with diesel fuel, further indicating low water content.

The GC-MS results are shown in Figure 3, they show that the bio-oil contained significant levels of ketone, phenols, and aromatics, which is consistent with fast-pyrolysis-derived oils.

This particular bio-oil product also showed significant levels of ethyl acetate and naphthalene. Another feature is that the acid concentration is much lower than what is typically observed for pyrolysis oils.

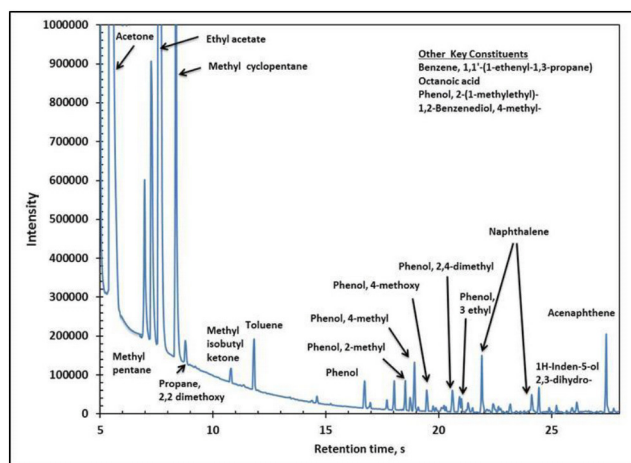


Figure 3. GC-MS results for the bio-oil.

The relative concentrations of these primary components were not determined but estimates were established by assuming equal concentrations (20 percent by volume) of the aromatics, phenols, ketones, ethyl acetate, and naphthalenes. This estimate is not unreasonable as most bio-oils contain concentrations ranging from 10 to 20 percent for phenols, acetones, aromatics, acids. In many cases the phenols are the predominant component class.

### Solubility Analysis

A preliminary solubility assessment was performed by exaggerating the concentration of one or more of these five components relative to the others to examine the subsequent effect on the resulting solubility curves (i.e. the solubility distance results as a function of bio-oil content in diesel) for each plastic type. For each bio-oil component, their corresponding Hansen solubility parameters are listed in Table 3. (Also included in the table are the parameters for a bio-oil composed of equal amounts of each component.) It is important to note that the parameter values for toluene and naphthalene are similar. Ethyl acetate and ketone have similar dispersive and hydrogen-bonding parameters, though polarity parameter is much higher for ketone. Phenol has similarities to the other components, except for hydrogen bonding. Because many of these component

parameters are similar to each other, the effect of their relative concentrations was not expected to significantly impact the resulting solubility curves for each plastic type.

The preliminary study showed that the relative shapes of the solubility curves were not dramatically affected. In most cases the shape (relative change in solubility distance) was essentially the same, but the position was shifted to higher (or lower values). For a few materials, the location of minimum solubility distance was shifted to higher bio-oil concentrations, but these shifts were on the order of 10 to 20%. Given that the resulting solubility curves were not highly dependent on the component concentrations (within the 10 to 20% range), a first order approximation of a bio-oil solubility parameter was made using equivalent concentrations of ketone, phenol, aromatic, ethyl acetate, and toluene. The resulting parameters are listed in the bottom row in Table 3.

Table 3. Hansen Solubility Parameters for Key Bio-oil Components

Component	Hansen Solubility Parameters		
	Dispersive	Polarity	Hydrogen
Ethyl acetate	15.8	5.3	7.2
Phenol	18.0	5.9	14.9
Ketone	15.5	10.4	7.0
Toluene	18.0	1.4	2.0
Naphthalene	19.2	2.0	5.9
Bio-oil	17.3	5.0	7.4

A more detailed solubility analysis was performed for each of the plastic materials and is presented in this paper. The analytical approach was based on the Flory-Huggins model using the Hansen solubility parameter (HSP) methodology. This type of analysis is useful in predicting swelling behavior in polymeric materials exposed to known solvents. The solubility behavior for each material was assessed by determining the solubility distance ( $d_s$ ) for each material type as a function of bio-oil content. Relative solubility for neat diesel and Bio20 was assessed by determining the solubility distance ( $d_s$ ) for each material type and comparing these values to the interaction radius (IR) of the polymer. The interaction radius represents the zone of high solubility for a given polymer and is independent of solvent type. If the solubility distance falls within (or is less than) the interaction radius (positive  $IR-d_s$  result), then moderate to high solubility can be expected depending on the value. Materials exhibiting distances roughly equivalent to the interaction radius would be expected to produce low to moderate solubility, while distances higher than the interaction radius (negative  $IR-d_s$  result) would predict negligible to low solubility. To facilitate discussion, the differences between the interaction radius and the calculated solubility distance for the materials in both test fuels are plotted graphically along with their general solubility curves.

The graphs and charts presented in this section were derived from the analysis as stated above. The Hansen solubility parameters were taken from the tables provided in *Hansen Solubility Parameters: A User's Handbook* [11]. The use of a single set of parameters for each plastic and fuel type means that the graphs will not have any error bars to indicate variability.

## Permeation Barriers

The solubility curves for the four barrier plastic materials are shown in Figure 4. The solubility distances for PVDF, PPS, and PET were all observed to decrease with increasing bio-oil content indicating the volume swell should also increase with bio-oil content. PTFE differed from the other three by slightly decreasing in  $d_s$  when moving from 0 to 15% bio-oil. For concentrations higher than 15%, the solubility distance is shown to increase with concentration. At 20% the solubility distance is only slightly less than for neat diesel, which suggests that the volume changes for PTFE in neat diesel and Bio20 should be similar. At high bio-oil concentrations, the volume swell is expected to be lower than for lower bio-oil concentrations. This implies that PTFE (which is also commonly used as a seal material) may be more compatible with blends containing high bio-oil content. In fact, the analysis indicates that PTFE is actually more compatible with bio-oil than diesel fuel.

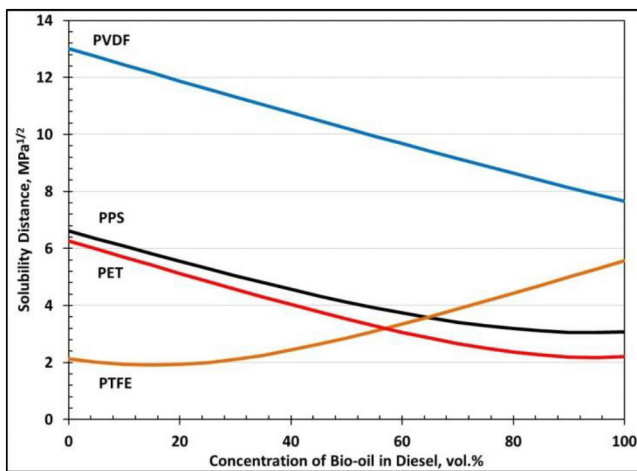


Figure 4. Solubility curves for the permeation barrier plastic materials.

The IR- $d_s$  results for the permeation barrier plastic materials with diesel and Bio20 fuels are depicted in Figure 5. The data indicate possible low to moderate solubility of either fuel to PPS, PET and PTFE, and low solubility with PVDF.

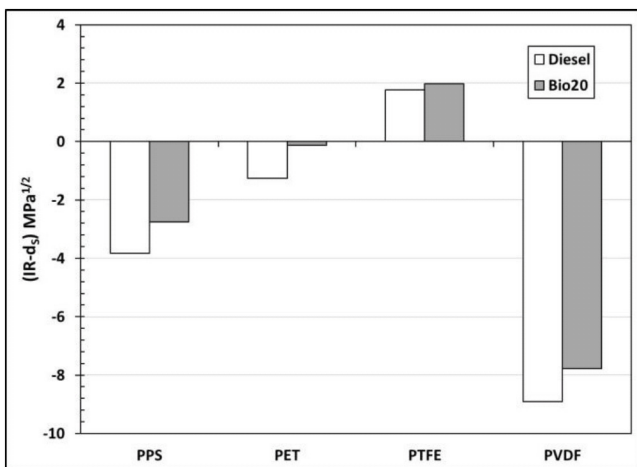


Figure 5. Chart showing IR- $d_s$  results for the permeation barrier plastic materials with neat diesel fuel and a blend composed of 20% bio-oil.

## Nylons and HDPE

The solubility curves for the four grades of nylon and HDPE are shown in Figure 6. The general shapes for the four nylon types are generally the same; all decrease with increasing bio-oil content. The solubility distance for HDPE, on the other hand, increases with bio-oil content. Based on these curves, the four grades of nylon will become more soluble as bio-oil is added to the baseline diesel fuel, but HDPE will become less soluble. The IR- $d_s$  results presented in Figure 7 indicate low solubility for the nylons with both diesel and Bio20. This figure also shows that, for HDPE, the interaction radius is only slightly less than the solubility distance, indicating that HDPE may exhibit moderate solubility (or volume swell) with these fuels.

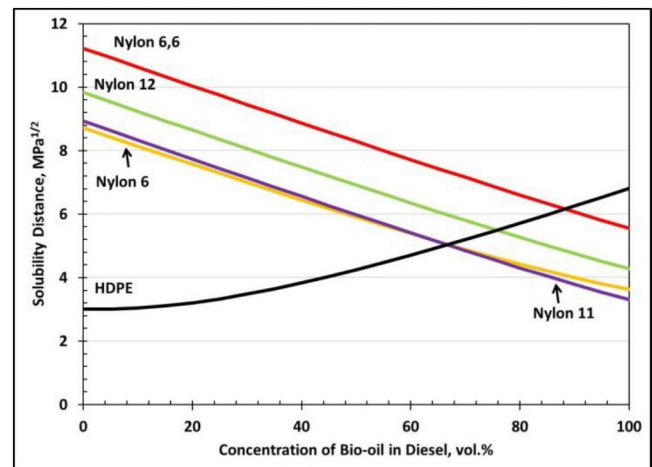


Figure 6. Solubility curves for the four nylon grades and HDPE.

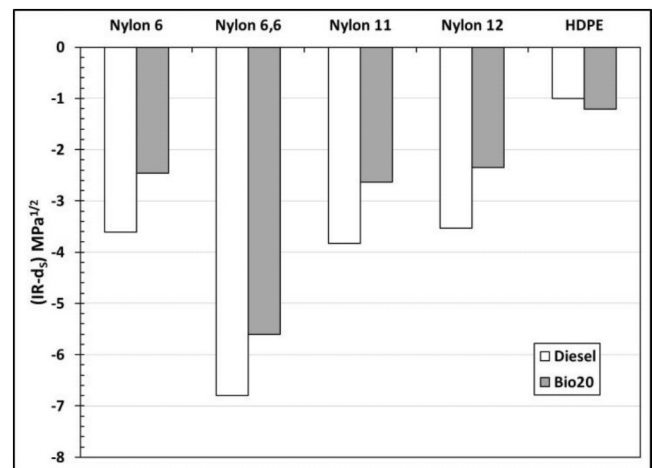


Figure 7. Chart showing IR- $d_s$  results for the four nylon grades and HDPE with neat diesel fuel and a blend composed of 20% bio-oil.

## Thermoplastic Resins

The two primary classes of thermoplastic resins evaluated in this study are polyester and vinyl ester resins. It is important to note that the authors of this paper were not able to directly obtain solubility parameters for the polyester resins. However, polyester resins are known to be highly soluble in ketone, which indicates that their solubility parameters are similar [15]. Because of this similarity, the solubility parameters for ketone were used for these resins in order to calculate the solubility distances and roughly determine behavior. The

solubility curves for each resin type are shown in Figure 8. Consistent with many other plastics the solubility (decreasing solubility distance) was observed to increase with increasing bio-oil content. The results in Figure 9 show that polyester resin can be expected to show modest solubility in diesel fuel and increased solubility with added bio-oil. The vinyl ester resin results suggest that the volume swell for this material should be lower than for the polyester resin.

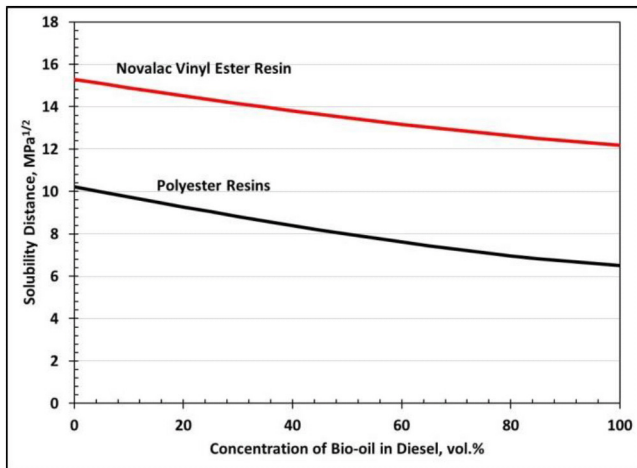


Figure 8. Solubility curves for the vinyl ester and polyester resins.

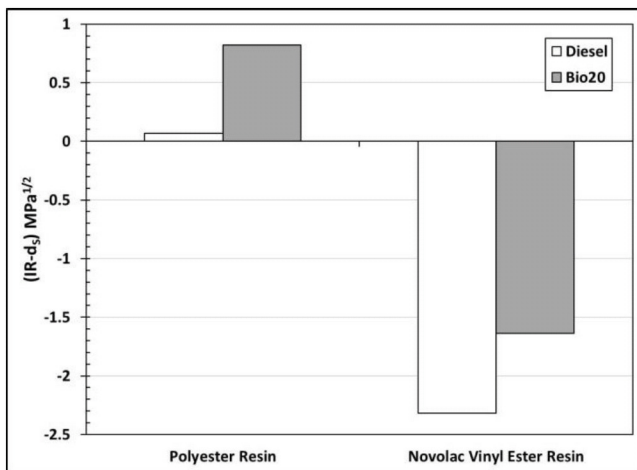


Figure 9. Chart showing IR- $d_s$  results for polyester and vinyl ester resins with neat diesel fuel and a blend composed of 20% bio-oil.

### Other Common Plastics

The solubility curves for other common plastic materials are shown in Figure 10. PTU, POM, and PBT all exhibit a linear decrease in solubility distance with added bio-oil content (solubility increases with bio-oil level). In contrast, polypropylene was observed to increase in solubility distance with increasing bio-oil concentration. PETG, which is a co-polymer of PET and ethylene glycol, exhibits a decrease in  $d_s$  when the bio-oil content is increased from 0 to 40%. Higher bio-oil concentrations were observed to produce an increase in  $d_s$ .

The IR- $d_s$  results for POM, PBT, PETG and PP are shown in Figure 11. Because an IR value for PTU was not found in the literature, it is not shown in this figure. The analysis suggests that POM and PBT

will exhibit moderate-to-high solubility (i.e significant volume swelling) in the two test fuels, and that PETG and PP will exhibit more modest levels of swell.

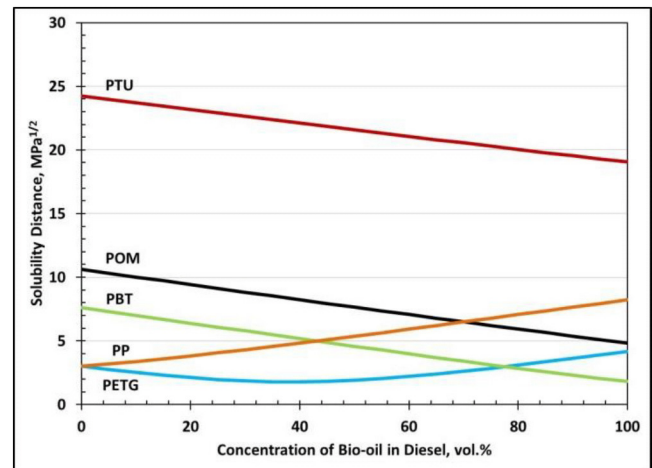


Figure 10. Solubility curves for other common plastics.

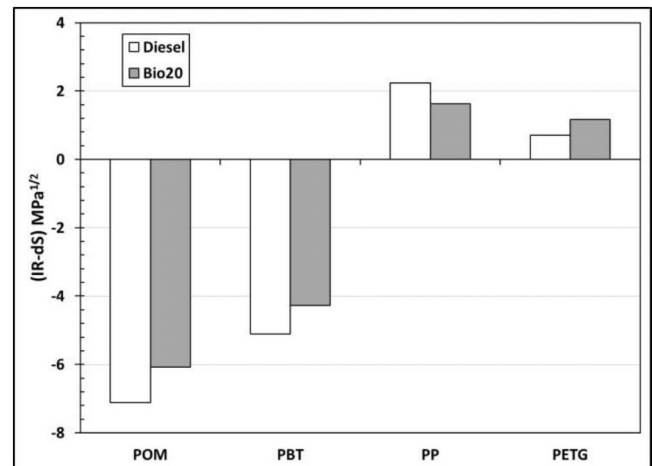


Figure 11. Chart showing IR- $d_s$  results for POM, PBT, PP, and PETG with neat diesel fuel and a blend composed of 20% bio-oil.

### Polymer Exposures to Diesel and Bio20

For each plastic material there were three specimens that were exposed to the test fuels. Each specimen was measured for volume and the presented results represent an average of the three specimens. The error is presented as the standard deviation. The hardness was measured at five locations on each specimen (each corner and at the center). As a result there are a total of 15 hardness measurements per material type. The error in hardness is also presented as a standard deviation.

### Permeation Barrier Materials

The wet volume results for the four permeation barrier plastic materials are shown in Figure 12. All four polymers exhibited negligible swelling with the neat diesel fuel. PPS, PET, and PTFE showed a slight volume increase when 20% bio-oil was added to the baseline fuel, but PVDF expanded over 15% (which is dramatic). The prior solubility analysis (as shown in Figures 4 and 5) was useful in

predicting the low swelling levels for PPS, PET, PTFE, but not for PVDF when exposed to Bio20. The reason for this discrepancy is unclear, but PVDF is known to be highly soluble with ketones. It is possible that the ketone level in the bio-oil is higher than estimated, but another explanation is that the ketone (or more specifically acetone which was present in the sample) may have been preferentially adsorbed by PVDF. Acetone has a smaller molecular size than most of the other bio-oil components, which would facilitate permeation into the PVDF structure. A key limitation of solubility theory is the inability to take into account molecular size and diffusivity. It is for that reason that small molecules such as water and methanol cannot be accurately studied using this approach.

As shown in Figure 13, PPS, PET, and PTFE were not dramatically affected by the drying process. However, for the PVDF specimen exposed to Bio20, the volume expansion dropped from 15.8% (when wetted) to 5% after drying. PVDF still retained fluid in its structure as evidenced by the 5% expansion from the original baseline condition. Fuel retention, following dryout, is not uncommon for many plastics and some elastomers [16]. Interestingly PVDF showed low volume swelling with gasoline test fuels containing ethanol or isobutanol [17].

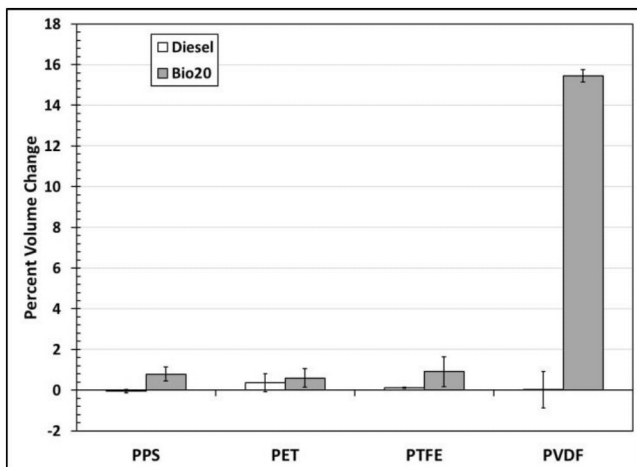


Figure 12. Wet volume change results for the permeation barrier plastic specimens.

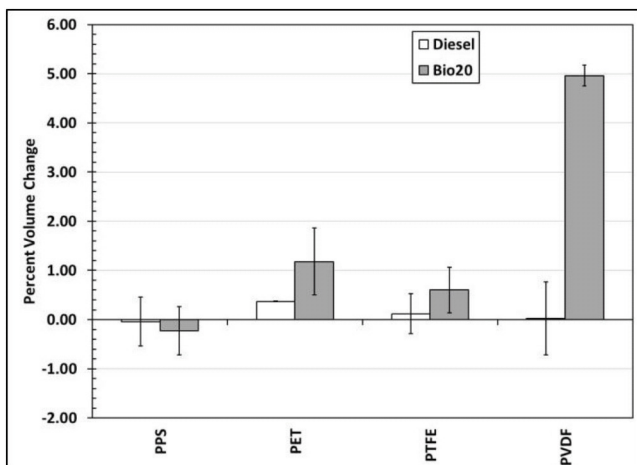


Figure 13. Volume change results for the permeation barrier plastic specimens after drying at 60°C for 65 hours.

The point change in hardness results for the permeation barrier plastics are shown in Figure 14 for the specimens in the wetted state and in Figure 15 after being dried for 65 hours at 60°C. PPS, PET, PTFE each exhibited essentially negligible change in hardness as demonstrated by the fact that the point changes are all within  $\pm 3$  points from the original baseline condition. This result is not surprising since the original volume changes (while in the wetted state) were low for these materials. Not surprisingly the PVDF specimen exposed to the Bio20 fuel was softened. The absorbed fuel (in the PVDF) provides no resistance to penetration and some level of softening proportional to the amount of swelling is to be expected.

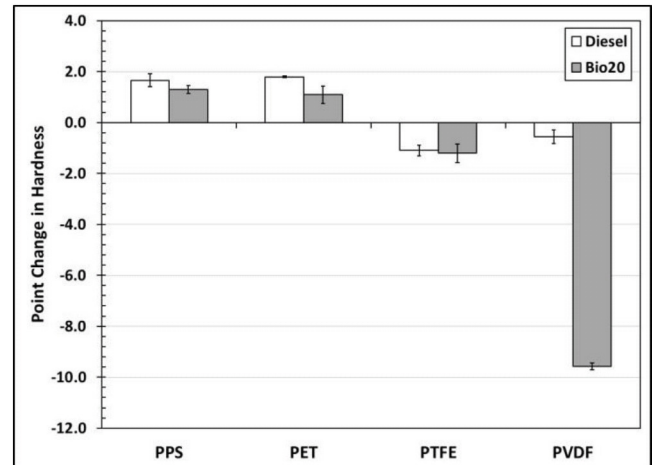


Figure 14. Point change in wet hardness results for the permeation barrier plastic specimens.

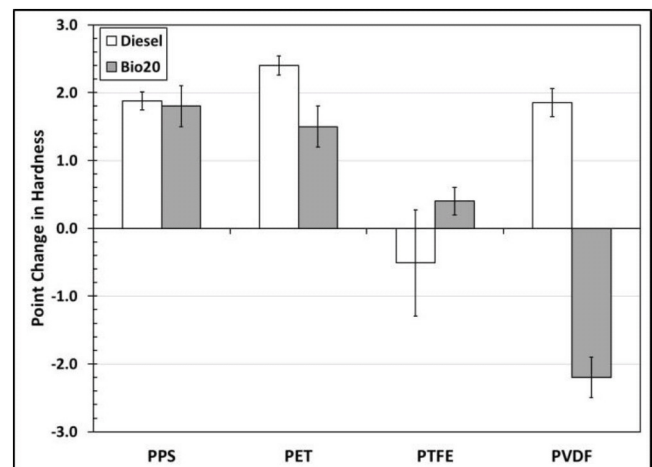


Figure 15. Point change in hardness results for the permeation barrier plastic specimens after drying at 60°C for 65 hours.

### Nylon and HDPE

The wet and dried volume changes for the nylon and HDPE specimens are shown in Figures 16 and 17, respectively. Interestingly, the petroleum-derived Nylon 6, Nylon 6,6, and Nylon 12 specimens exposed to the neat diesel fuel showed a small drop in volume for the wetted condition. (This volume loss was maintained even after drying.) Volume shrinkage indicates the removal of material from the original condition. One possibility is that the volume loss is due to the removal of absorbed water in the specimens. Nylons are known to



be highly water absorbent and the extent of absorption is roughly proportional to the level of water in the surrounding environment [18]. Since diesel fuel contains only minute quantities of water, the nylon would lose water to equilibrate with its surroundings. In contrast to diesel fuel, bio-oils typically contain appreciable quantities of water, and this higher concentration may have prevented water removal due to equilibration in the nylon. In fact the volume changes for the nylon specimens exposed to the bio-oil blend do not show a volume reduction in the wetted state.

It is important to note that Nylon 12 also exhibited significant volume loss following exposure to gasoline test fuels containing ethanol or isobutanol [17]. The volume of Nylon 11 (which is derived from vegetable oil) was unaffected by the baseline diesel fuel, but expanded over 4% when exposed to Bio20. This expansion was maintained in the dried state indicating significant fuel retention.

The results for Nylons 6, 6,6, and 12 approximated the predictions from the earlier solubility analysis, which suggested negligible to low volume change. The volume loss following exposure to neat diesel suggests a small level of polymer dissolution occurred, which offset any expansion caused by fuel permeation. The high level of swell observed in Nylon 11 specimens exposed to Bio20 was not anticipated by the solubility analysis. This discrepancy indicates that the Hansen solubility parameters used to represent Nylon 11 were not accurate for this particular formulation.

The solubility analysis predicted that HDPE performance would be similar for either test fuel and that modest swelling can be expected. The results in Figures 16 and 17 show that moderate swelling of HDPE did occur, but the extent of swelling for the specimens exposed to Bio20 was 8% (versus 4% for the neat diesel exposures). After drying the volumes remained expanded by 4% for both fuel types.

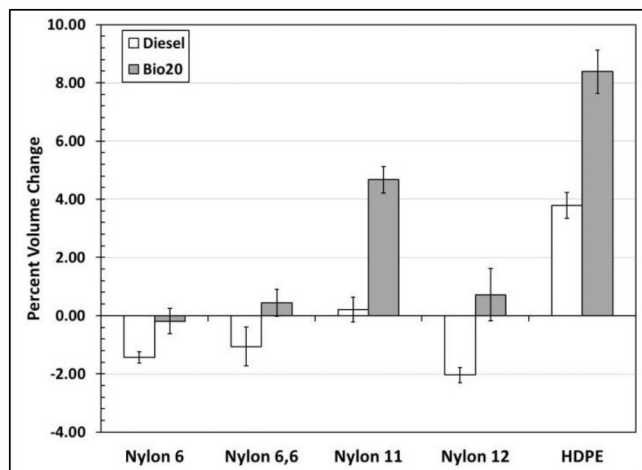


Figure 16. Wet volume change results for four nylons and one HDPE material.

The changes in hardness for these materials (shown in Figures 18 and 19) are relatively low, but there are a couple of noteworthy observations. Accompanying the slight increases in wet hardness for the Nylon 6 and Nylon 6,6 specimens were small volume contractions as shown in Figures 16 and 17. This slight embrittlement was also observed for the specimens exposed to the Bio20 fuel. The combination of volume contraction and hardness increase suggests extraction of a plasticizer, which is added to many polymers to improve pliability. This likely occurred for the specimens which were

also exposed to Bio20. However, the higher volume swell caused by the Bio20 may have masked plasticizer removal, which could only be detected by the hardness increase. Interestingly, the retained fluid in these specimens should have contributed to a hardness decline, but this effect was not noted.

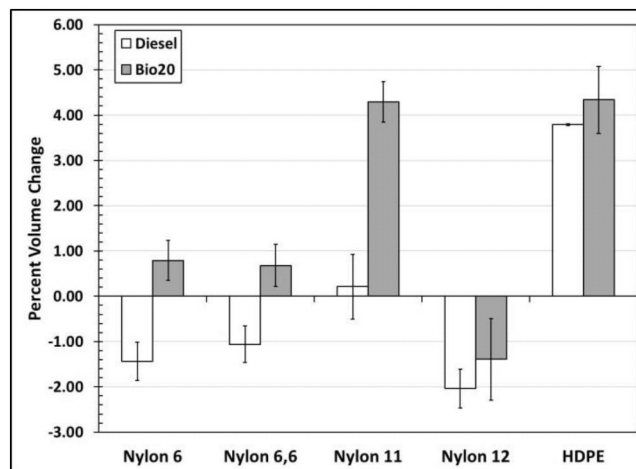


Figure 17. Volume change results for four nylons and one HDPE material after drying at 60°C for 65 hours.

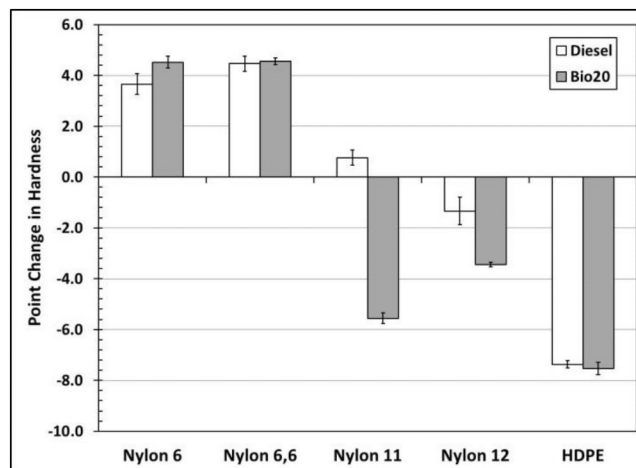


Figure 18. Point change in wet hardness results for four nylons and one HDPE material.

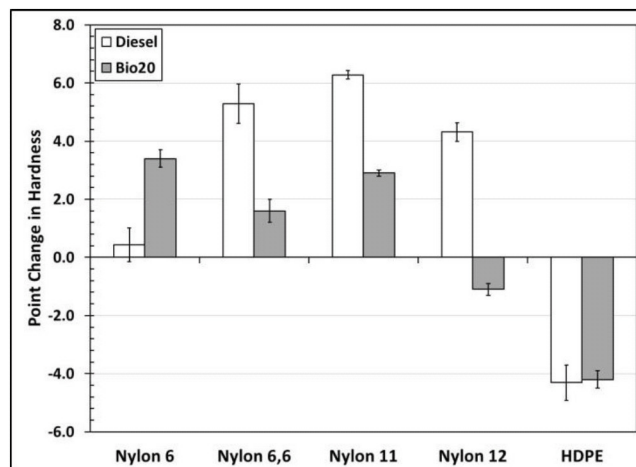


Figure 19. Point change in hardness results for four nylons and one HDPE material after drying at 60°C for 65 hours.

Nylon 12 also contracted with exposure to either test fuel, however the hardness did not increase as would be expected with plasticizer dissolution and removal. It is conceivable that another additive type may have extracted or the nylon itself may have experienced some small level of dissolution. When dried, the Nylon 12 specimens showed a slight hardness increase with the diesel fuel exposure, which when compared to the corresponding shrinkage suggests plasticizer extraction.

Nylon 11 hardness was unaffected by the baseline diesel but showed modest softening with the added bio-oil. HDPE also exhibited modest softening and for both of these materials the hardness decline is consistent with volume expansion caused by fuel adsorption. When compared to the baseline hardness measurements of the unexposed samples (not shown), these results are actually considered low. Nylon 11 also experienced a small amount of embrittlement following dryout.

### Thermoplastic Resins

The volume change results for the four thermoplastic resins are shown in Figures 20 and 21 for the wetted and dried conditions, respectively. The two isophthalic resin types are further identified as 1:1 and 1:2 according to the ratio of isophthalic acid to maleic anhydride used to formulate each resin. Negligible volume change was noted for each resin type exposed to the neat diesel fuel. In contrast, exposure to Bio20 resulted in significant expansion for the four resins. When dried, resins volumes remained swelled, albeit to a lower degree. The newer, more advanced, resin formulation (Novolac vinyl ester) exhibited the lowest swell, while the 1:1 isophthalic legacy resin expanded the most of the four types.

It is important to note that these same materials were also included in a previous study, which evaluated their compatibility performance in gasoline test fuels containing low level of ethanol and isobutanol [16,17]. These resins exhibited higher volume expansion (2-10%) in a gasoline baseline fuel and even higher swelling (20-25%) when exposed to gasoline containing intermediate (10-20%) levels of either ethanol or isobutanol.

The solubility analysis was useful in predicting higher solubility with the Bio20 fuel and that the polyester resins would exhibit higher swelling than the vinyl ester. It is important to keep in mind; however, that the parameters for ketone were used for the polyester resins.

The solubility analysis was not useful for predicting the performance of the Novolac vinyl ester resin. It indicated that the Novolac vinyl ester would exhibit low solubility (swell) with the Bio20 fuel. However, the actual swell for this fuel-polymer combination was over 10%, which is higher than expected. This discrepancy may be the result of inaccurate parameters for the bio-oil. More accurate HSPs for the bio-oil would better define the extent of solubility (or swelling).

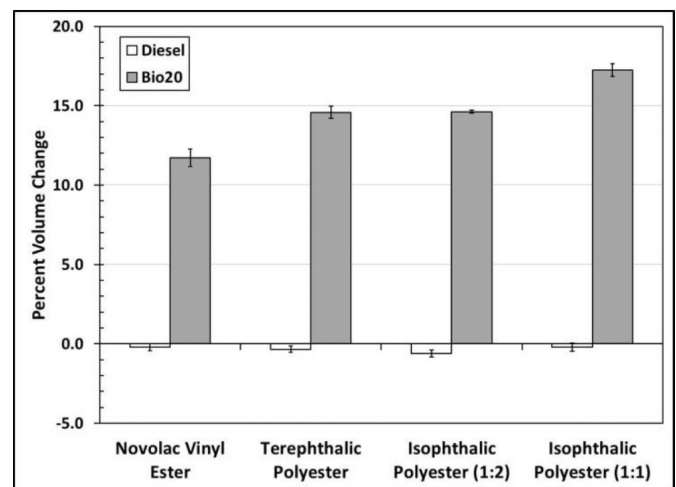


Figure 20. Wet volume change results for four fiberglass resins.

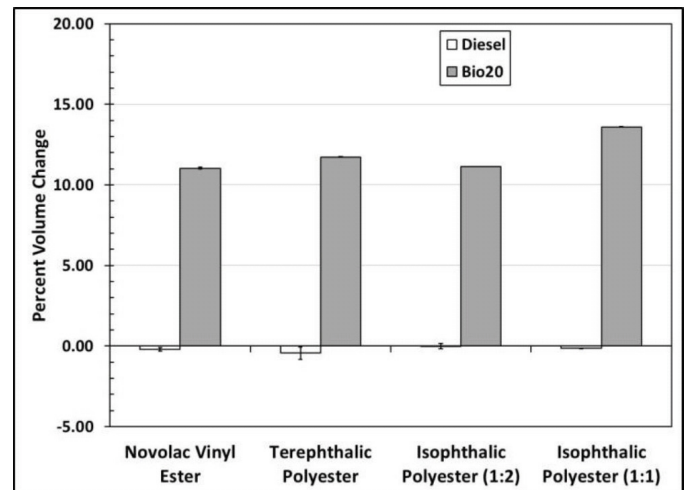


Figure 21. Volume change results for four fiberglass resins after drying at 60°C for 65 hours.

The resulting change in hardness from the original condition is shown in Figure 22 for the wetted resin specimens and in Figure 23 after drying for 65 hours at 60°C. The drop in hardness (softening) corresponds to the observed volume swell across the resin types. No change in hardness was noted for the specimens exposed to the neat diesel fuel, indicating good compatibility. The resin specimens exposed to the Bio20 test fuel remained softened after drying due to fuel retention in the resin. The degree of softening in the polyester resins is significant. However it is important to keep in mind that, in actual practice, these resins are almost always reinforced with high loadings of glass fibers. The high modulus of elasticity of the reinforcing fibers prevents the overall structure from expanding and deforming.

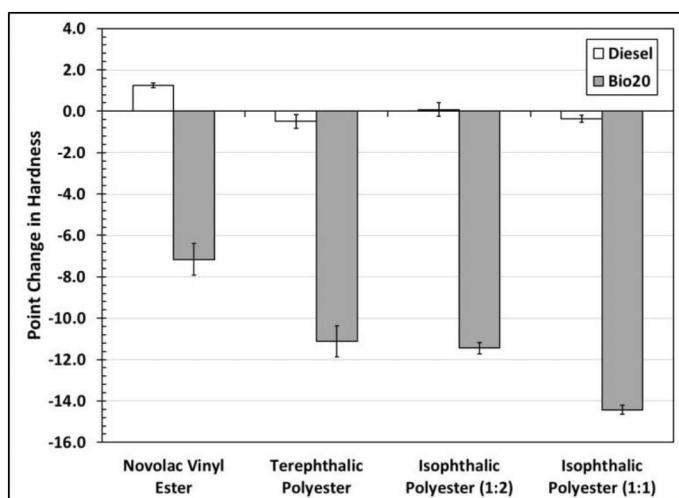


Figure 22. Point change in wet hardness results for four resin materials.

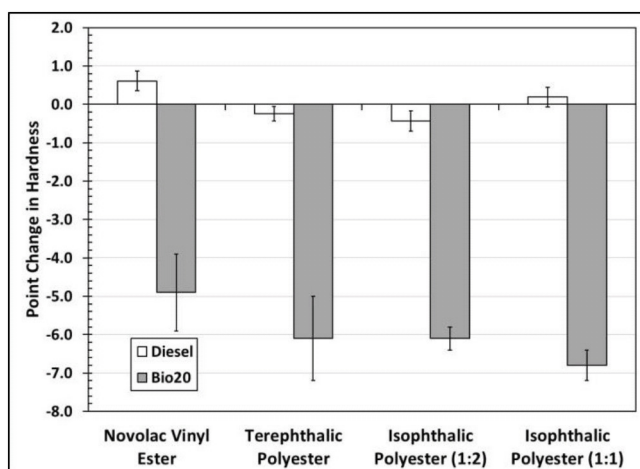


Figure 23. Point change in hardness results for four resin materials after drying at 60°C for 65 hours.

### Other Common Plastics

Their volume change results for other common plastics following test fuel exposure are shown in Figure 24. The dried volume changes shown in Figure 25 parallel the wet volume results and indicate high fuel retention with the Bio20 test fuel. The wet volume changes for the two acetals (POM and POM copolymer) were negligible for the neat diesel exposures and were a modest 3% following exposure to Bio20. The solubility analysis (shown in Figures 10 and 11) predicted low solubility (swell) for acetal in either test fuel. The volume swell for acetal was also expected to be higher for the blend containing bio-oil. The volume of PBT was also unaffected by the neat diesel fuel. Similar to acetal, there was a small increase (5%) with exposure to Bio20. The solubility analysis accurately predicted that PBT would exhibit more swell than the acetals.

The solubility curves also indicated that PP would swell more than the acetals and PBT as demonstrated in Figure 24. The extent of volume swell was relatively high and similar for both test fuels. Interestingly, the solubility analysis had also predicted that PP would swell more in the baseline diesel fuel than in Bio20, but the opposite had occurred as the volume swell was slightly higher for the

specimens exposed to the Bio20 test fuel. The reason for this discrepancy is attributed to inaccuracies surrounding the solubility parameters for both the fuel and polypropylene.

The PETG specimens were essentially unchanged following exposure to the baseline diesel fuel, but swelled to over 15% when exposed to the Bio20 test fuel. This result was not anticipated by the solubility analysis, which predicted a more similar performance between the two fuels. PETG differed from many of the other polymers in that it is a co-polymer of PET (which exhibited low solubility) and ethylene glycol. The high volume swell suggests that the ethylene glycol may be responsible for the differences between the solubility analysis and the observed test results.

Because an interaction radius could not be found for PTU, no pre-analysis was performed. The results in Figure 24 show that PTU may have lost volume slightly when exposed to diesel fuel (but the error bars indicate that this volume change may be statistically insignificant). In contrast this material did experience significant swelling when exposed to Bio20. Interestingly, the data obtained from the PTU specimens was more varied than the other plastics as evidenced by the larger error bars.

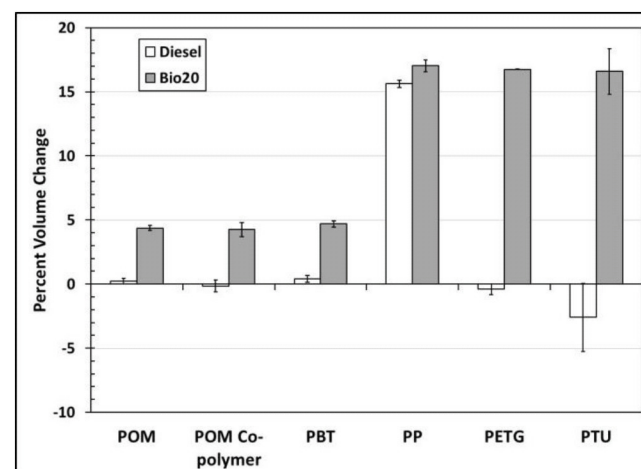


Figure 24. Wet volume swell results for other common plastics.

When the specimens were dried, those that had swelled during the liquid exposures all exhibited fuel retention as indicated by the dried volume change results in Figure 25. The acetals, PBT, PP and PTU did shrink a modest amount when going from the wetted to the dried state, but PETG maintain the same volume expansion in the dried state as it did in the wetted.

The wetted and dried hardness results for the other common plastics are shown in Figures 26 and 27, respectively. POM, POM copolymer, and PBT all showed slight softening consistent with fuel retention for the specimens exposed to Bio20. PP and PETG exhibited softening that corresponded to their volume swell results. PTU was unusual in that it exhibited a pronounced hardness increase for the sample exposed to the diesel fuel. Significant hardness increase (while wetted) is a strong indicator that some level of plasticizer extraction occurred. This result implies that PTU (like many plastics) was compounded with a plasticizer which was extracted during the exposure. This plasticizer removal would also account for the slight

loss in volume. Interestingly, when exposed to Bio20, the PTU specimens incurred high volume swell and softening. The retained fuel in PTU is quite high and can be expected to provide enough softening to more than offset any hardness increase associated with plasticizer extraction that may have occurred.

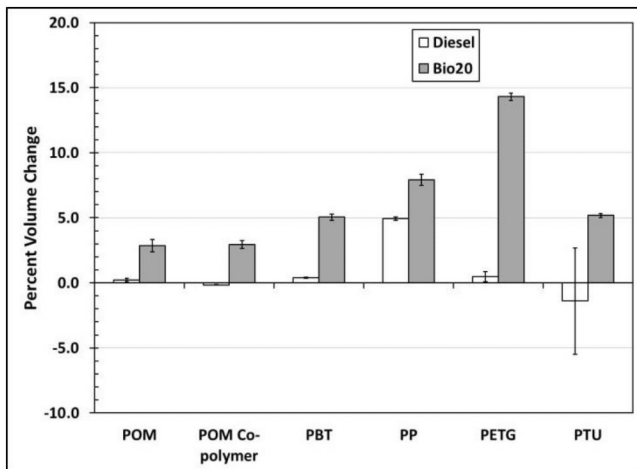


Figure 25. Volume change results for other common plastics after drying at 60°C for 65 hours.

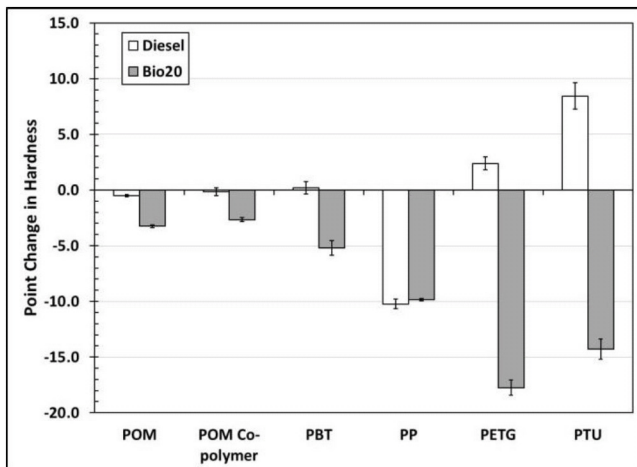


Figure 26. Point change in wet hardness results for other common plastic specimens.

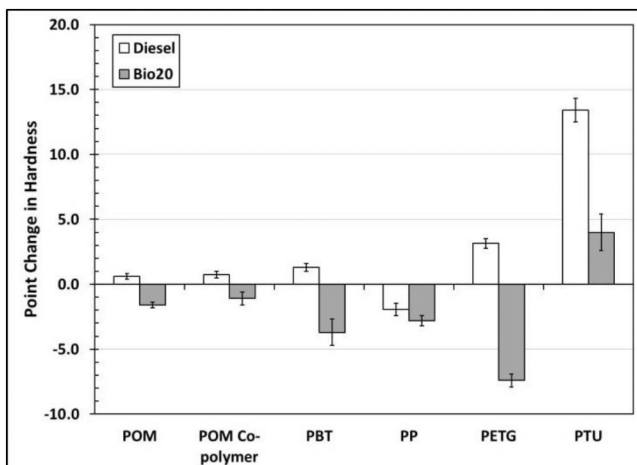


Figure 27. Point change in wet hardness results for other common plastic materials after drying at 60°C for 65 hours.

## DISCUSSION

It is important to keep in mind when considering the results that only one type of bio-oil was evaluated in this study. The chemistry of bio-oils produced either via fast pyrolysis or other processes are known to vary widely. Because much of bio-oil development and production is still in the research stage, the quantities available are very small (usually less than 1 liter). These small quantities prevent comprehensive polymer compatibility experimentation. The reason that the bio-oil type used in this study was chosen was that it came from a supplier who could produce it in quantities approaching 15 liters. The investigators realized that this particular bio-oil may not have an ideal representative chemical composition, but it did serve as a basis for polymer compatibility and hopefully will serve as a baseline to compare other studies with. Interestingly, the solubility analysis showed that, for the primary components, the solubility parameters do not differ considerably within the compositional range of other fast-pyrolysis-derived bio-oils. The similarity of the solubility parameters would indicate that, perhaps, the results provided in this paper, may in fact be representative of bio-oils, in general.

The performance for the plastic materials investigated in this study varied according to type. For most materials, the solubility analysis was good at predicting the swell results, but for several materials, it was not effective. The presence of a small, highly mobile molecule like acetone has the potential to render the solubility study ineffective, but outside of a few plastics, it did not have too much of an impact. The impact of the bio-oil and diesel fuel on the plastics was quite different from the results obtained for these materials with ethanol and gasoline. For example, PVDF was much more compatible with gasoline-ethanol blends than with bio-oil. On the other hand, mid-level blends of ethanol in gasoline caused the isophthalic fiberglass resins to fracture and several of the nylons to degrade, but they remained intact in the bio-oil and diesel test fuels. Interestingly PTU performed poorly in all of the biofuels tested to date. A summary table relating material type to its impact and anticipated performance is included as an [Appendix](#) in this paper.

## SUMMARY/CONCLUSIONS

In spite of some notable exceptions, the Hansen solubility analysis generally provided good to excellent agreement to the observed volume swell for many of the plastic materials. Except for HDPE and PP, the remaining plastic materials exhibited little to no volume change when exposed to the baseline diesel test fuel. The initial indication is that those materials showing negligible volume change are compatible with diesel fuel. This is not necessarily the case, as the PTU specimen experienced a notable hardness increase from the diesel exposure even though it did not swell, which suggests that a plasticizer additive had been extracted by the diesel test fuel.

Exposure to Bio20 did not affect the PPS, PET, and PTFE, Nylon 6, Nylon 6,6 and Nylon 12 specimens, but the other materials showed noticeable volume swell and softening. In all of these cases, the specimens remained swollen even after drying for 65 hours at 60°C. This result is consistent with fluid retention. Interestingly PVDF, which is another common permeation barrier material, underwent pronounced swelling (over 14%) when 20% bio-oil was added to the

baseline diesel. In earlier studies [17], PVDF showed good compatibility with bio-derived alcohols and this result was not anticipated by the solubility analysis.

The three petroleum-derived nylons (Nylon 6, Nylon 6,6, and Nylon 12) were unusual in that they experienced a slight contraction when exposed to diesel fuel, which was not observed with the Bio20 exposures. Contraction cannot occur without dissolution and, because it was accompanied by a corresponding hardness increase, suggests that plasticizer extraction had occurred. HDPE swelled to 4% in the baseline diesel fuel and over 8% with exposure to Bio20. When dried the volume expansion remained at 4% for the HDPE specimens exposed to the baseline diesel fuel. Interestingly, the volume expansion for the specimens exposed to Bio20 dropped to 4%.

The four fiberglass resins were unaffected by the diesel test fuel, but they expanded over 10% when exposed to the bio-oil blend. This level of expansion is much lower than that exhibited following exposure to alcohol-blended gasolines [16,17]. A hardness decrease accompanied the volume expansion.

The acetals (POM and POM co-polymer) and PBT were also unaffected by the baseline diesel fuel. These materials did show a modest (~4%) volume expansion and softening following exposure to Bio20. PP swelled approximately 15% and softened appreciably in either test fuel. These results suggest that PP (like HDPE) is primarily impacted by the baseline diesel fuel than by the added bio-oil.

PETG and PTU were highly impacted by the added bio-oil. The volume and hardness for PETG was not affected by the baseline diesel test fuel, but when 20% bio-oil is added the volume increased 15% with a corresponding drop in hardness. Since PET (the primary co-polymer of PETG) was unaffected by these test fuels, the observed property changes must be due to ethylene glycol (which is the other co-polymer). PTU showed a small drop in volume and hardness increase with exposure to diesel indicating that plasticizer extraction may have taken place. The Bio20 test fuel produced a 5% increase in volume and significant softening in this material.

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## ACKNOWLEDGMENTS

This effort was sponsored by the U. S. Department of Energy, Office of Biomass LLC. The test facilities and protocol were established from an earlier investigation that had been sponsored by the Biomass, Clean Cities and Vehicle Technology Programs within the US DOE's Office of Energy Efficiency and Renewable Energy. The authors gratefully acknowledge their support. Oak Ridge National Laboratory is a multi-program laboratory operated by UT-Battelle for the U. S. Department of Energy under contract DE-AC0500OR22725.

## DEFINITIONS/ABBREVIATIONS

**ASTM** - American Society for Testing and Materials

**B20** - diesel fuel containing 20% biodiesel

**Bio20** - test fuel composed of 80% off-highway diesel fuel and 20% bio-oil

**d<sub>s</sub>** - solubility distance

**DMA** - dynamic mechanical analysis

**DOE** - US Department of Energy

**E10** - gasoline containing 10% ethanol

**E15** - gasoline containing 15% ethanol

**EPA** - US Environmental Protection Agency

**FRP** - fiber-reinforced plastic

**HDPE** - high density polyethylene

**HSP** - Hansen solubility parameter

**IR** - interaction radius

**LMW** - low molecular weight

**ORNL** - Oak Ridge National Laboratory

**PBT** - polybutylene terephthalate

**PET** - polyethylene terephthalate

**PETG** - PET copolymer

**POM** - polyoxymethylene

**PP** - polypropylene

**PPS** - polyphenylene sulfide

**PTU** - polythiourea

**PVDF** - polyvinylidene fluoride

**SAE** - Society of Automotive Engineers

**APPENDIX**

Summary Table for Material Performance and Impact with Bio20

Material type	Application	Observed Impact of Bio20 Fuel	Possible Significance and Impact
PPS	Permeation barrier for fuel transport piping	Negligible	Appears acceptable for use with Bio20 fuel.
PET	Permeation barrier for fuel transport piping	Negligible	Appears acceptable for use with Bio20 fuel.
PTFE	1. Permeation barrier for fuel transport piping 2. Multiple seal applications	Negligible	Appears acceptable for use with Bio20 fuel.
PVDF	Permeation barrier for piping	High volume swelling and softening	Not compatible with Bio20*. Existing piping subject to damage and leakage.
Nylon 6	1. Plastic fuel piping walls 2. Fuel line seal	Negligible	Appears acceptable for use with Bio20 fuel.
Nylon 6,6	1. Plastic fuel piping walls 2. Fuel line seal	Negligible	Appears acceptable for use with Bio20 fuel.
Nylon 11	1. Plastic fuel piping walls 2. Permeation barrier 3. Some sealing applications	Volume expanded over 4%	Modest volume expansion indicates permeation of Bio20 can be expected. Its use in flexible piping should be limited to outer wall material only. Some legacy flexible piping systems may be subject to buckling and possible damage with Bio20*.
Nylon 12	1. Plastic fuel piping walls 2. Permeation barrier 3. Some sealing applications	Negligible	Appears acceptable for use with Bio20 fuel.
HDPE	Structural piping material used in fuel transport	Volume expanded over 8%	Not compatible with Bio20 as a structural component if placed in direct contact.* Since HDPE is used primarily as outer wall reinforcement, piping containing HDPE should be fine for use with Bio20.
Novolac vinyl ester	Resin material for rigid FRP piping	Volume expanded to ~12%	Not compatible with Bio20 in pure resin form.* Most likely acceptable in FRP piping systems. No impact is predicted.
Terephthalic polyester	Resin material for rigid FRP piping	Volume expanded to ~15%	Not compatible with Bio20 in pure resin form.* Most likely acceptable in FRP piping systems. No impact is predicted.
Isophthalic polyester (1:2)	Resin material for rigid FRP piping	Volume expanded to ~15%	Not compatible with Bio20 in pure resin form.* Most likely acceptable in FRP piping systems. No impact is predicted.
Isophthalic polyester (1:1)	Resin material for rigid FRP piping	Volume expanded to ~17%	Not compatible with Bio20 in pure resin form.* Most likely acceptable in FRP piping systems. No impact is predicted.
POM	Fuel lines and fuel tank components	Modest swelling (5%)	Acceptable in sealing and flexible hose/piping systems. May be less durable as a rigid structural component.
POM Co-polymer	Fuel lines and fuel tank components	Modest swelling (5%)	Acceptable in sealing and flexible hose/piping systems. May be less durable as a rigid structural component.
PBT	Limited use in fuel supply systems	Modest swelling (5%)	Acceptable in sealing and flexible hose/piping systems. May be less durable as a rigid structural component.
PP	Limited use in tanks and pumps	High swelling in both diesel and Bio20	Since the performance in Bio20 was similar to diesel fuel, no impact is expected for systems exposed to diesel fuel.
PETG	No fuel applications were noted for this material	Very high swelling (over 15%)	Not recommended for use with Bio20.* No impact is expected since this material is not normally used in fuel systems.
PTU	Fuel system coating	High volume expansion	Coatings exposed to Bio20 will likely be compromised. May promote corrosion in coated metal systems.

\*While the results show that the Bio-oil type evaluated in this study was not compatible, it is quite possible that some bio-oils do have acceptable compatibility performance.