

Effects of Biodiesel on Plastics

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Abstract

Many chemicals have the ability to attack plastics leading to failure. In some cases, the source of the chemical is not well defined. In this study, the effect of biodiesel, a fatty acid methyl ester, on various plastics, namely polyamide 6 (PA 6), polycarbonate (PC), acrylonitrile-butadiene-styrene (ABS) and ABS/PC plastic blends was studied. Various feedstocks of biodiesel were also studied, including, soy bean oil (new and used), animal fat (tallow), corn oil as well as choice white grease. The plastics samples were tested following an ASTM standard where a predefined strain is applied to the samples prior to exposure to the solvent (biodiesel). This study has shown that biodiesel can be incompatible with engineering plastics, such as PC, ABS and ABS/PC blends.

Introduction

In the recent decade, there has been a continued rise of biofuel production in the United States due to the fluctuations of petroleum costs and negative impacts of fossil fuels to the environment. This has demanded the creation of a more sustainable energy resource such as bioethanol and biodiesel. The biodiesel industry, in particular, has produced more than 1 billion gallons in 2011 [1]. The U.S. National Biodiesel Board has noted that it is a key milestone for the industry. As of August 2012, there are about 699 million gallons biodiesel produced according to the U.S. Energy Information Administration [2]. Currently, there are 105 biodiesel plants in U.S. with an annual production capacity of 2.1 billion gallons. It is expected that these numbers will continue to increase as new feedstocks resources are explored.

The use of vegetable oils in diesel engines was considered inadequate due to its high kinematic viscosity, which can lead to engine fuel deposits. Vegetable oils have to be reduced to a lower viscosity before it can be used as a diesel fuel. One of the methods to obtain this is by transesterification. In the presence of a catalyst (acid, base or enzyme), triglycerides in oils reacts with an alcohol (typically methanol is used), to produce biodiesel or fatty acid methyl esters (FAME) and glycerol. This involves three reversible stepwise chemical reactions that convert triglycerides to diglycerides to monoglycerides, then finally to glycerol. Each step releases one mole of FAME. The transesterification process decreases the viscosity

significantly, correspondingly giving the biodiesel a viscosity that is low enough to be used in diesel engines.

Standard #2 diesel fuel is a liquid diesel fuel derived from petroleum. It is mainly composed of saturated hydrocarbons and aromatic hydrocarbons. To be used as substitute for #2 diesel fuel, biodiesel needs to meet ASTM D6751 and EN14214 before it can be used as a substitute for standard #2 diesel. These standards give detailed requirements (e.g. flash point, water and sediment content, other contaminant levels) that the fuel must meet.

Biodiesel fuel is made from a reaction of triacylglycerides and methanol. The resulting biodiesel is essentially fatty acid methyl esters (FAME), as shown in Figure 1. It is known that many plastics will have incompatibility issues with ester-based chemicals [3]. The study investigated the compatibility of various plastics to six biodiesels formulated from different feedstocks.

Chemical Degradation

Chemical degradation of plastic by a foreign material involves the reduction in length of the molecular chain and corresponding molecular weight of the polymer. It is generally observed that the longer the molecular chains of the plastic, the more desirable the mechanical properties, as well as other properties [4]. This is primarily due to the entanglement of the long molecular chains. Chemical degradation involves a chemical reaction where the molecule is modified and effectively reduced in length.

Environmental Stress Cracking

Environmental stress cracking (ESC) involves stress and a foreign chemical synergistically working together to break molecular secondary bonds of the plastic [5]. ESC is different than chemical degradation since it does not reduce the length of the molecules. The chemical penetrates the molecular structure with the assistance of stress and interferes with intermolecular forces allowing for molecular disentanglement to take place.

ESC is an accelerated form of brittle plastic creep. It is associated with sustained stress over a period, involves molecular disentanglement and results in the plastic cracking in a brittle mode. The chemical associated with ESC accelerates the molecular disentanglement. Figure 2 shows a typical time to failure for a plastic. As the stress is reduced failure (cracking) takes longer to occur. In this

graph two transitions are shown: brittle-to-ductile and ductile-to-brittle failure modes. The effect of a chemical that can cause ESC to occur is to shift this graph to the left, effectively reducing the time to failure at the same stress.

Assessment of Chemical Compatibility

Experimental data may be found on chemical resistance of some plastics to a number of biodiesels, however, very little will be found on ESC. To evaluate the ability of a plastic to perform while exposed to a foreign material, appropriate testing should be completed. It is important that the tests be run over a period of time to allow the fluid and application of stress/strain interact with the plastic. As stated above, ESC is essentially an accelerated form of plastic creep in a brittle mode. Following an ASTM standard [6,7,8] one can evaluate the compatibility of a plastic while subjected to stress.

Effect of Biodiesels on Plastic

Test Procedure

To analyze several different plastic materials to various formulations of biodiesel, as well as, standard #2 diesel fuel, ASTM D 543 was used. The plastic samples were placed in a jig that applied a constant strain of 1.5% over a 10 day period, as shown in Figure 3. Samples were also exposed to the standard diesel and biodiesels at zero applied strain. A strain of 1.5% is on the higher of strains that are typically used for ESC testing. To ensure a constant exposure of the plastic to the chemical, a cotton gauze was wrapped around a two-inch section of the sample for the chemical to be applied to. Testing was done at ambient conditions. The samples were observed on a daily basis and chemical reapplied as necessary. The samples were analyzed by visually observing cracking. Time for cracking to occur gave a comparative measure of the severity of the chemical.

Plastic Materials Analyzed

Four different plastic materials were tested. The samples were molded under controlled conditions by Standard Plaque in Melvindale, Michigan.

Polyamide 6 (PA6)

DSM Alkulon
K222-D Natural
Unreinforced

Polycarbonate (PC)

LG-Dow
Calibre 301-22 Clear
Unreinforced

Acrylonitrile-butadiene-styrene (ABS)

BASF Terluran
GP-22 Natural
Unreinforced

PC/ABS

Sabic Cycoloy
CX7240 white
Unreinforced

Biodiesel Blends

Ten biodiesel samples were obtained from Renewable Energy Group (REG) (Ames, Iowa). The samples were produced using the following feedstocks: used cooking oil, soy, tallow, distiller's corn oil, choice white grease (CWG), and mixed feedstocks¹. The biodiesel samples were analyzed using gas chromatography (GC). Table 1 shows the fatty acid (FA) and FAME composition of the samples. There were too many minor GC peaks to positively identify, thus only the five major peaks were presented. Additionally, tallow biodiesel have many other minor FAs or GC impurities outside the five major FAs, so the total GC peaks accounted by the five major FAs is low (mid 80%). It also has more unsaponifiable matter, which is reflected by the relatively low total FAME in the sample.

Sample #3

Source: Used cooking oil
Date: 8/17/2009

Sample #6

Source: Soy
Date: 9/11/2012

Sample #7

Source: Mixed feedstock
Date: 7/5/2012

Sample #8

Source: Tallow
Date: 9/11/2012

Sample #9

Source: Choice white grease (CWG)
Date: 8/16/2009

Sample #10

Source: Distillers corn oil
Date: 9/11/2012

¹ Note, samples 1,2,4,5 were repeats of the other samples, but produced on a different date. Thus, they were not tested.

Table 1 FAME and Fatty acid composition of biodiesel samples

Sample	Fatty Acid (FA), %				
	16:0	18:0	18:1	18:3	18:3
3	13.5	4.8	25.9	49.1	6.8
6	10.8	4.3	21.9	54.5	8.5
7	22.3	11.7	41.8	22.5	1.6
8	28.8	25.8	41.1	3.9	0.3
9	24.8	9.6	51.9	13.0	0.7
10	14.2	2.8	29.0	52.8	1.2
	FAME, % in sample, as received		Total GC peak accounted by the 5 FAs, %		
3	95.2		96.2		
6	98.6		97.8		
7	97.4		91.8		
8	92.7		84.0		
9	95.6		91.0		
10	99.8		91.7		

Samples 3, 6, 7, 8, 9, 10 are as follows respectively, used cooking oil, soy, mixed feedstock, tallow, choice white grease, and distillers corn oil.

Discussion

The results of ESC testing are shown in Table 2. There are several general conclusions that can be made from the tests that were performed. It should be noted that the results are for the specific materials tested and should not specifically be applied to plastics of the same type. Molecular weight of the plastic is a driver on how well the plastic will perform when a subjected to a chemical and/or stress.

1. The strained (1.5%) PA 6 did not crack when subjected to the biodiesel or standard diesel fuels.
2. The strained PC, ABS and PC/ABS were affected greatly by the biodiesel fuels. The PC and PC/ABS sample cracked nearly instantly when the biodiesel was applied to the strained samples (Figure 4). The fracture surface was indicative of environmental stress cracking with multiple crack initiation sites and crack progression in a brittle mode (Figures 5 and 6).
3. The strained ABS did not crack when subjected to the standard diesel fuel.
4. The strained PC was slightly affected by the standard diesel fuel with surface hazing taking place (Figure 7).
5. The strained PC/ABS cracked over a 5-hour period when subjected to standard diesel fuel.

The samples were also subjected to each biodiesel with no stress applied (i.e. pure chemical attack analysis) and to a constant 1.5% strain with no chemical applied (i.e. creep

analysis). In both of these conditions none of the samples cracked or showed any signs of microcracking or hazing.

Table 2 – Effect of Biodiesel Fuels to Plastic – Cracking Time.

Biodiesel	Plastic			
	PA 6	PC	ABS	PC/ABS
#3	No cracking	< 60 sec	~ 12 hours	< 60 sec
#6	No cracking	< 60 sec	~ 12 hours	> 60 sec
#7	No cracking	< 60 sec	~ 12 hours	> 60 sec
#8	No cracking	< 60 sec	~ 12 hours	> 60 sec
#9	No cracking	< 60 sec	~ 12 hours	> 60 sec
#10	No cracking	< 60 sec	~ 12 hours	> 60 sec
Standard Diesel	No cracking	Slight surface hazing	No cracking	Cracked in about 5 hours

Conclusions

The use of renewable fuels is on the rise. Biodiesel has a tremendous upside due to the number of sources where this fuel can be derived. An understanding of the compatibility of these fuels on the plastics needs to be understood to avoid unexpected failures. This will help ensure this important resource does not gain a reputation as damaging plastic parts. The chemical structure of biodiesel is nearly all fatty acid methyl esters, which many plastics are not compatible. This study showed a number of strained plastics that failed when exposed to biodiesel. Some of these same plastics had little to no effect when exposed to standard #2 diesel fuel.

References

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5. J. Jansen, "Environmental Stress Cracking – The Plastic Killer," *Advanced Materials & Processes*, June (2004).
6. ASTM D 543 - Standard Practices for Evaluating the Resistance of Plastics to Chemical Reagents.
7. ASTM D 1693 - Standard Test Method for Environmental Stress-Cracking of Ethylene Plastics.
8. D.C. Wright, *Environmental Stress Cracking of Plastics*, Rapra (2001).

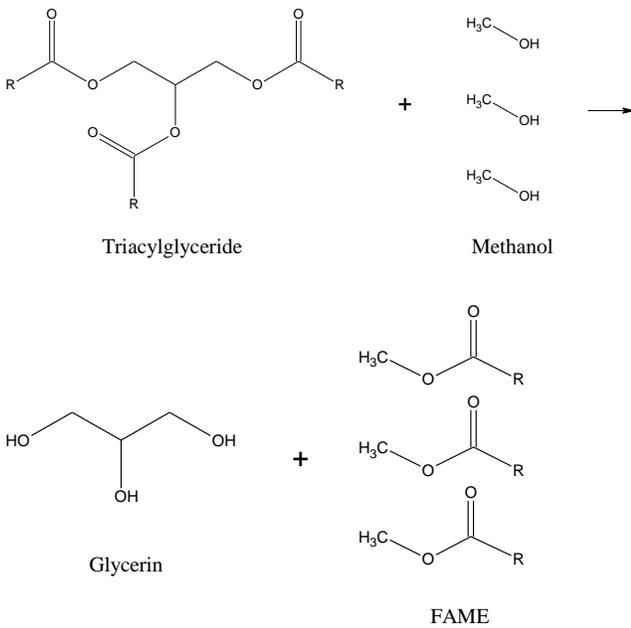


Figure 1 – Transesterification reaction of triglyceride to biodiesel

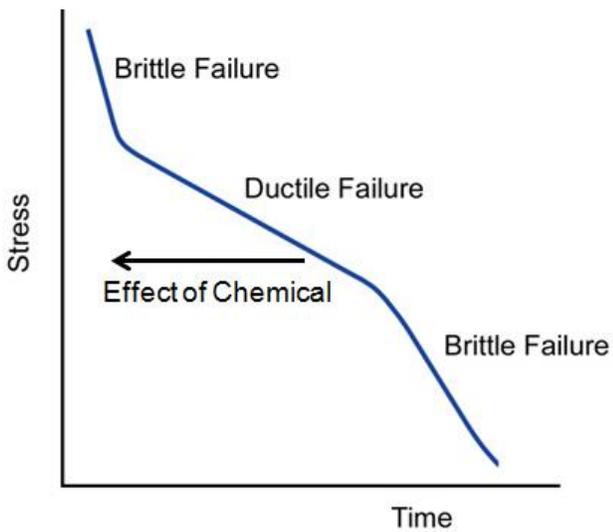


Figure 2 – Effect of a chemical to the time to failure for a plastic.

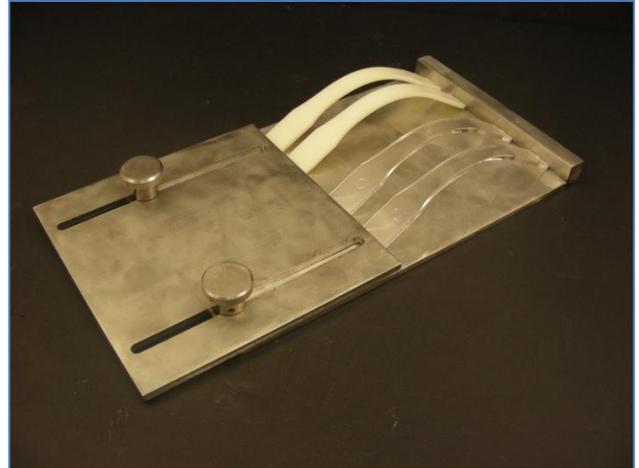


Figure 3 – A constant strain jig used for environmental stress cracking.

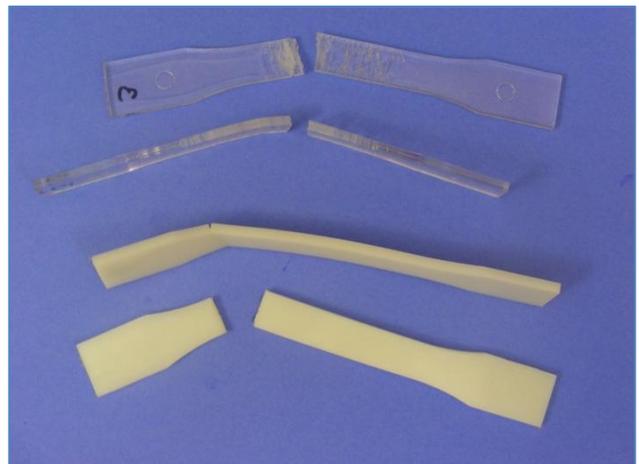


Figure 4 – Polycarbonate and Acrylonitrile-butadiene-styrene samples after exposure to biodiesel and 1.5% strain.

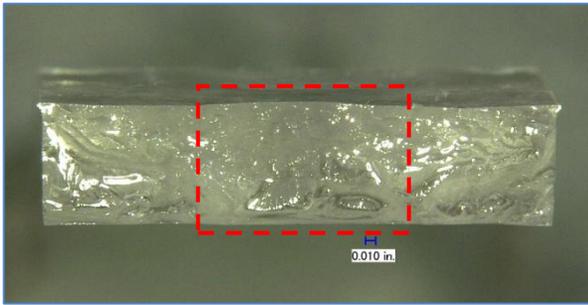


Figure 5 – Fracture surface of a polycarbonate sample after exposure to biodiesel and 1.5% strain.

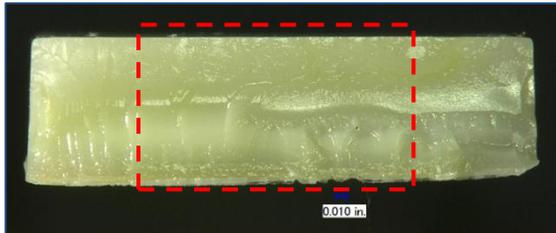


Figure 6 – Fracture surface of an Acrylonitrile-butadiene-styrene sample after exposure to biodiesel and 1.5% strain.

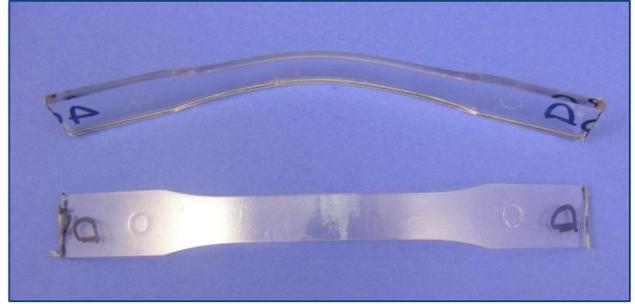


Figure 7 – Polycarbonate samples after exposure to standard #2 diesel and 1.5% strain.