Compatibility of polyethylene grades with biofuels and biodiesel-heating oil blends

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Summary

Biofuels including ethanol and biodiesel (fatty acid methyl ester) represent an important renewable fuel alternative to petroleum-derived transport fuels. Increasing biofuels use would bring some benefits, such as a reduction in oil demands and greenhouse gas emissions, and an improvement in air quality. Materials compatibility is a major concern whenever the fuel composition is changed in a fuel system. The aim of this work is to study the interaction between high density polyethylene (HDPE) grades and biofuels such as E85 (fuel with 85% ethanol), E10 (fuel with 10% ethanol), biodiesel and B10 (heating oil with 10% biodiesel). 10 l jerricans made of two different polyethylene grades were filled with these fuels and exposed to temperatures of 20°C and 40°C for more than one year. Some of the jerricans for filling with B10 were fluorinated at the inner layer to prevent permeation. Tensile properties (tensile strength, breaking elongation and elasticity modulus) and Melt Flow Rate (MFR) were determined once a month, and FTIR-spectroscopy was used to evaluate possible changes. The tensile properties tensile strength and breaking elongation of HDPE jerrican cuttings decreased, but not significantly, after immersion in E10, E85, biodiesel and B10. In particular, the elasticity modulus of the polyethylene grades was reduced after exposure to all test fuels. The FTIR spectra of HDPE jerrican cuttings showed that the immersion tests for 14 months with E85 at 20°C and 40°C only caused an increase in the peak of 1585 cm⁻¹ (C=C stretching vibrations) in the chemical structure of HDPE. The FTIR spectra of HDPE jerrican cuttings showed that immersion tests for 18 months with biodiesel at 20°C and 40°C led to a broadening of the C=O peak of 1740 cm⁻¹ and the appearance of the hydroxyl group at 3500 cm⁻¹. Both features are explained by secondary degradation products of the polyethylene decomposition process caused by the temperature and unsaturated fatty acid content in the biodiesel since biodiesel decomposes quickly at elevated temperatures. The broadening of the C=O peak to 1740 cm⁻¹ can be attributed to aldehyde carbonyl and ester carbonyl groups mutually overlapping. Measurements of the melt flow rate (MFR) showed an increase in the MFR with the immersion time in biodiesel due to the unsaturated fatty acid content. Diffusions of oxygen and rapeseed methyl ester increase the chemical impact on polyethylene grades.
1 Introduction

Biofuels including ethanol and biodiesel (fatty acid methyl ester) represent an important renewable fuel alternative to petroleum-derived transport fuels. Increasing biofuel use would bring some benefits, such as a reduction in oil demands and greenhouse gas emissions and an improvement in air quality. Ethanol has become one of the main fuel components as it complies with environmental regulations. Biofuels have great advantages due to their physical and chemical characteristics, raw materials and production costs. However, they also have some disadvantages, mainly in terms of their compatibility with materials.

Alcohol is able to dissolve organic materials. Although E10 and E85 fuels have different concentrations of ethanol, both of them can dissolve the petroleum-based sediment, particulates and lacquers found in fuel tanks previously used for gasoline or diesel fuel. In this case, E85 has a greater solvent capability than E10. Although the mechanism is not really understood, the presence of ethanol in fuel facilitates the permeation of hydrocarbons through certain thermoplastics. Permeation refers to the mass transport of a substance (or solvent) through a membrane that is driven by a chemical potential or activity gradient. Diluted ethanol in an E10 fuel possesses sufficient chemical potential or activity to become the chemical gradient permitting permeation through the material. Of course, permeation depends on several factors, such as solvent-material interaction, the surface-area-to-thickness ratio of the non-metal, and the degree of cross linking (e.g., elastic contraction) in a material. However, the same principles do not necessarily hold true for thermoplastics - materials that have very little to no cross-linking – and the lack of cross-linking can affect the rate of permeation. The permeation of gasoline or ethanol through a polymer can result in a change in the physical, chemical and mechanical properties of a polymer. For example, permeation can result in excessive swelling. Polymers also face an issue where excessive permeation and swelling can lead to plasticization. In some cases, chemicals such as antioxidants and heat stabilizers are added to polymers to confer certain performance properties. Since these additives are not chemically bound, excessive swelling in a material can eventually lead to the extraction of these plasticizers as the solvent passes through the material. This will lead to a measurable loss in the strength and flexibility of the polymer.

Biodiesel is defined as a fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils such as raps oil. It is produced by a reactive chemical process called transesterification. In this process vegetable oil food stocks react with short chain alcohols (typically methanol) and a catalyst (typically sodium or potassium hydroxide). In essence, the triglyceride ester is broken down into glycerol and three alkyl esters by substituting three mono-functional alcohol molecules for the tri-functional glycerol. The biodiesel is refined by washing and filtrating to remove any excess unreacted alcohol, catalyst or glycerol. Biodiesel is also added to heating oil such as B10.

Regarding the compatibility with polymers, most of the research has been published on the swelling phenomenon and degradation in the mechanical properties of elastomers. The auto-oxidation, hygroscopic nature, higher electrical conductivity, polarity and solvency properties of biodiesel cause degradation in elastomers [1]. Considering other types of polymeric materials, such as the polyethylene used in automotive tanks, few published papers such as that by Maru et al. can be found on the compatibility of biofuels and polyethylene [2]. One conclusion of this paper is that the
ageing of biodiesel did not cause degradation of HDPE after an immersion time of 125 days at 60 °C.

The study by Baena et al. compared the effects of gasoline and E20 on various polymeric materials typically used in auto parts. The mass increases of HDPE when immersed in both fuels were similar because of their affinity in terms of polarity [3].

The time-dependent sorption of biodiesel in a typical polyethylene for container application was investigated in comparison to conventional diesel fuel at 40 °C, 50 °C and 60 °C by Böhning et al. [4]. Changes in impact strength as determined by the Charpy method were further characterized in more detail by analyzing the fracture surfaces.

HDPE has been proving its worth as an economical blow moulding material not only for automotive tanks for many years. High-quality hollow technical articles made of HDPE have proved their value as dangerous goods packagings a million times over. Our former studies about the interaction between high density polyethylene (HDPE) grades and biofuels such as E85 (fuel with 85 % ethanol) and biodiesel showed:

The tensile properties of HDPE jerrican cuttings decreased, but not significantly, after immersion in E85 and biodiesel for one year. In particular, the elasticity modulus of the polyethylene grades was reduced after exposure to biodiesel [5, 6].

The present work investigates the interaction between biofuels (E10, E85 and biodiesel) and B10 and polyethylene grades at 20 °C and 40 °C to determine the MFR and tensile properties for two years. FTIR spectroscopy after an exposure time of more than one year was also used. The aim of the exposure tests with B10 in HDPE packagings with and without a fluorine permeation barrier for two years was to test the damaging effect of the biodiesel content in the heating oil.

2 Experimental procedure

2.1 Exposure tests with biofuels

10 l jerricans made of two different HDPE grades, called types A and B in this paper, were used for the exposure tests. HDPE type A is a material with a high density and relatively high degree of crystallinity and is used to represent brittle failure. It is commonly used for drums. HDPE type B is a material with a lower degree of crystallinity and is commonly used for Intermediate Bulk Containers (IBCs).

The jerricans were filled with E85 and biodiesel made of rapeseed and exposed to temperatures of 20 °C and 40 °C for 14 months (E85) and 18 months (biodiesel). Only jerricans made of type A were filled with E10 and only jerricans made of type B were filled with B10. The inner layer of some of the jerricans filled with B10 was fluorinated to prevent permeation. These jerricans were exposed to temperatures of 20 °C and 40 °C for 30 months (E10) and three years (B10).

2.2 Determination of MFR

The MFR was determined according to the international standard ISO 1133 [7]. It is defined as the material quantity in grams flowing at a defined pressure and temperature over 10 minutes through a capillary of defined dimensions. The MFRs of material taken from the 10 l jerricans’ side walls were determined before and after different storage times with the biofuels at 20 °C and 40 °C.
2.3 Determination of tensile properties

The tensile properties (tensile strength, breaking elongation and elasticity modulus) were determined according to EN ISO 527-2: “Determination of tensile properties – Part 2: Test conditions for moulding and extrusion plastics” with tensile testing equipment [8].

Sheets were cut from the side walls of 10 l jerricans before and after storage with the biofuels at 20 °C and 40 °C. At least five test specimens were cut from the sheets, each with a length of 110 mm and a breadth at the end of 12.5 mm. The length and the breadth of the narrow parallel part were 25 mm and 4 mm respectively.

It should be noted that the thickness of the test specimens varied from 1.4 to 1.6 mm, a difference which must be considered when interpreting the results.

2.4 FTIR analysis

FTIR-spectroscopy is perhaps the most widely used spectroscopy technique because of its versatility in determining the composition, conformation and crystallinity of polymers [9]. This testing method is often used for polymer fingerprints since comparison of characteristic absorption bands in the IR spectrum can lead to identification of the bonds and functional groups present in the polymer. Therefore, it is possible to monitor if any chemical changes occur in the polyethylene matrix. 150 µm microtom slices from the jerrican’s walls were prepared after pre-storage with E10, E85, biodiesel and B10. The equipment used was an FTIR spectrometer specially designed for research whose basic configurations can be altered by the user.

3 Results

3.1 Change in the MFR and tensile properties in E10

Berlanga-Labari et al. performed immersion tests of high density polyethylene in E5 (fuel with 5% ethanol) and E10 for 2000 h at 45 °C. They observed a slight variation of the mechanical properties, but no effects on the chemical structure and physical properties of polyethylene [10]. The test duration of the present exposure tests was longer and led to the following conclusions:

The MFR is a material parameter for the oxidative degradation of polyethylene grades. Measurements of the MFR of polyethylene grade A test specimens cut from the jerrican wall showed an increase in the MFR after 30 months exposure of the jerricans to E10. This increase differed only minimally at 20 °C and 40 °C. The MFR increased by 19% at 20 °C and by 21% at 40 °C. Therefore the oxidative degradation of grade A was still low after 30 months exposure to E10 (see Table 1).

Table 1: Change in MFR of polyethylene grade A according to immersion time in E10 at 20 °C and 40 °C

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Immersion time (no. of months)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0 10.48 2 10.33 4 10.33 6 10.56 8 10.7 10.84 10 10.86 12 10.97 14 11.00 16 11.12 18 11.14 20 11.25 24 11.32 30</td>
</tr>
<tr>
<td>40</td>
<td>0 10.48 2 10.20 4 10.34 6 10.42 8 10.82 10 10.95 12 10.98 14 11.22 16 11.25 18 11.35 20 11.32 24 11.45 30 11.50</td>
</tr>
</tbody>
</table>

The mechanical properties of polyethylene are influenced by the degree of crystallinity, which depends on the total degree of branching along the PE molecule. The particular behaviour of polyethylene is due to the fact that the macromolecules
do not react only spontaneously to mechanical strain. Individual molecular chains seek to reduce the imposed loading stresses until an equilibrium value [11].
The measured tensile strength values showed an insignificant increase of 5% at 20 °C and 9% at 40 °C after 14 months of exposure. Afterwards the tensile strength values decreased again. After 30 months the measured values decreased by 1% (5%) of the initial value at 20 °C (40 °C).
The breaking elongation values slightly increased by 4% at 20 °C and 5% at 40 °C after 30 months exposure to E10 (see Figure 1).

A higher reduction in the measured values of the modulus of elasticity (E-modulus) was observed after 30 months exposure to E10. The E-modulus values of grade A decreased by 60% at 20 °C and by 67% at 40 °C (see Figure 2).
3.2 Change in the MFR and tensile properties in E85

Measurements of the MFR of test specimens cut from the jerrican wall showed for both polyethylene grades an increase in the MFR after 14 months exposure of the jerricans to E85, whereby this increase differed only minimally at 20 °C and 40 °C. The MFR of grade A increased by 23% and that of grade B by 16% at 40 °C after 14 months exposure to E85. It has to be noted that a higher increase in the MFR for grade B was already measured after one month exposure to E85. This distinctive increase in the MFR was determined for grade A after two months exposure (see Table 2). Therefore, it can be stated that the oxidative degradation of both grades was still low after 14 months exposure to E85. The reason for the increase in the MFR is the decrease in crystallinity due to the reduction in the crystalline regions as a result of interactions of the fuel with the polymer. The grades are affected by ageing because of not only the impact of the substance but also the influence of the temperature.

Table 2: Change in MFR of polyethylene grades A and B according to immersion time in E85 at 20 °C and 40 °C

<table>
<thead>
<tr>
<th>Grade</th>
<th>MFR (g/10 min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Immersion time (no. of months)</td>
</tr>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>A 20 °C</td>
<td>9.48</td>
</tr>
<tr>
<td>A 40 °C</td>
<td>9.48</td>
</tr>
<tr>
<td>B 20 °C</td>
<td>6.45</td>
</tr>
<tr>
<td>B 40 °C</td>
<td>6.45</td>
</tr>
</tbody>
</table>

The measured tensile strength values of test specimens cut from the jerrican wall made of grade A after exposure to E85 for 14 months at 20 °C (40 °C) increased by 16%. A 2% (4%) increase in the tensile strength for test specimens made of grade B was determined. The measured values showed an insignificant decrease in the tensile strength of both grades in the first months, especially at 40 °C. The tensile strength values increased again from the seventh month (see Figure 3).

Figure 3: Change in tensile strength (left) and breaking elongation (right) of polyethylene grade A according to immersion time in E85 at 20 °C and 40 °C
The measured breaking elongation values varied more than the measured tensile strength values. A minimal increase in breaking elongation, similar to tensile strength, was measured for grade B after 14 months at 20 °C and 40 °C. The breaking elongation was reduced in the first months of exposure and increased again in the eighth month. The breaking elongation of grade A increased by 6% after 14 months at 40 °C. After the first few months a decrease in the breaking elongation was measured for this grade too (see Figure 3).

A reduction in the measured values of the modulus of elasticity (elastic modulus) was observed in the first few months for the two grades at both 20 °C and 40 °C. The elastic modulus of grade A even decreased by 50%. The elastic modulus values of grade A increased again with the sixth month of exposure to E85 and reached 82% of the value without exposure after 14 months at 40 °C. 96% of the basic value was determined for grade B at 40 °C. The basic value represents the elastic modulus value before exposure of the polyethylene grades to E85 (see Figure 4).

3.3 Change in the MFR and tensile properties in biodiesel

During exposure of jerricans made of both grades to biodiesel clearly visible oxidative degradation took place: the higher the MFR, the higher the oxidative degradation. Increases in the MFR of 54% for grade A and 43% for grade B were measured after 18 months at 20 °C. An increase in the MFR of 52% for grade A after 18 months at 40 °C was proof of this degradation. The MFR of grade B could not be determined due to the high oxidative damage. Blistering was observed on the outside wall of jerricans made of grade B (see Table 3).

Table 3: Change in MFR of polyethylene grades A and B according to immersion time in biodiesel at 20 °C and 40 °C

<table>
<thead>
<tr>
<th>Grade</th>
<th>MFR (g/10 min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Immersion time (no. of months)</td>
</tr>
<tr>
<td></td>
<td>0  1  2  3  4  5  6  7  8  9 10 11 12 14 18</td>
</tr>
<tr>
<td>X</td>
<td>MFR was not measurable</td>
</tr>
</tbody>
</table>
The biodiesel impact resulted from the presence of free radicals driven by diffusion of oxygen and methyl ester. The biodiesel itself was subject to an ageing process by the formation of unsaturated fatty acids such as linoleic acid or linolenic acid [12]. Both the short and long term mechanical properties of polyethylene are dependent on the molecular weight and degree of branching of the polymer. The tensile strength values of test specimens cut from the jerrican walls were slightly reduced for both grades in the first months at 20 °C and 40 °C and increased again after six months. An increase of 13% was determined for grade B after 12 months at 40 °C. Longer exposure time of 18 months reduced the tensile strength values of grade A and B again. Grade B test specimen lost 29% of the tensile strength basic value at 40 °C. This grade especially became more brittle due to higher oxidative degradation (see Figure 5).

![Figure 5: Change in tensile strength (left) and breaking elongation (right) of polyethylene grades A and B according to immersion time in biodiesel at 20 °C and 40 °C](image)

![Figure 5: Change in tensile strength (left) and breaking elongation (right) of polyethylene grades A and B according to immersion time in biodiesel at 20 °C and 40 °C](image)

The breaking elongation values were subject to variations due to differences in the wall thickness of the jerricans. It was evident for this material parameter too that the breaking elongation of both grades was slightly reduced in the first months and increased again afterwards. The maximum increase in the breaking elongation of 6% was determined for grade A after 12 months at 40 °C. Afterwards the breaking elongation values were reduced again, especially the values for grade B which lost 40% of the basic value after 18 months at 40 °C (see Figure 5). The values of the elastic modulus were reduced by 57% for grade A and 53% for grade B after 18 months exposure to biodiesel at 40 °C. The reason was the progressive oxidative degradation of the polyethylene grades.

### 3.4 Change in MFR and tensile properties in B10

The MFR values could only be determined for jerrican cuttings without a fluorinated inner layer. The increase in the MFR differed only minimally at 20 °C and 40 °C after 3 years. The MFR increased by 45% at 20 °C and 48% at 40 °C. B10 contains 10% biodiesel. Unfortunately, these values cannot be compared with those values after exposing jerricans of grade B with pure heating oil. This relatively high increase in the MFR is comparable to the increase in the MFR in pure biodiesel. The MFR could not
be determined after 18 months exposure of the jerricans with pure biodiesel at 40 °C (see Table 4).

**Table 4:** Change in MFR of polyethylene grade B according to immersion time in B10 at 20 °C and 40 °C

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>MFR (g/10 min)</th>
<th>Immersion time (no. of months)</th>
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<tbody>
<tr>
<td>20 °C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.32</td>
<td>7.65</td>
<td>8.25</td>
</tr>
<tr>
<td>7.87</td>
<td>8.33</td>
<td>8.54</td>
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<tr>
<td>8.33</td>
<td>8.56</td>
<td>8.98</td>
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<tr>
<td>8.77</td>
<td>8.94</td>
<td>9.03</td>
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<tr>
<td>9.03</td>
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<td>9.04</td>
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<tr>
<td>9.04</td>
<td></td>
<td>9.14</td>
</tr>
<tr>
<td>24 °C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.32</td>
<td>7.70</td>
<td>8.38</td>
</tr>
<tr>
<td>7.97</td>
<td>8.45</td>
<td>8.55</td>
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<tr>
<td>8.38</td>
<td>8.82</td>
<td>8.94</td>
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<tr>
<td>8.89</td>
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<td>9.12</td>
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<td>9.14</td>
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</table>

A smaller decrease in the tensile properties was visible due to the influence of the permeation barrier. The tensile strength values of grade B test specimens without a permeation barrier were reduced by 18% (19%) and with a permeation barrier by 3% at 20 °C and 40 °C (see Figure 6).

![Figure 6](image_url)

**Figure 6:** Change in tensile strength (left) and breaking elongation (right) of polyethylene grade B according to immersion time in B10 at 20 °C and 40 °C

The breaking elongation values in Figure 7 showed the same tendency. A reduction of the breaking elongation was measured of 2% (8%) for grade B test specimens without a permeation barrier and of 1% (5%) for those with a permeation barrier at 20 °C (40 °C).

![Figure 7](image_url)

**Figure 7:** Change in tensile strength (left) and breaking elongation (right) of polyethylene grade B according to immersion time in B10 at 20 °C and 40 °C

The E-modulus serves as a measure of stiffness. The E-modulus values of test specimens without a permeation barrier was reduced by 40% (50%) and the E-modulus
values of test specimens with a permeation barrier by 9% (15%) at 20 °C (40 °C). The permeation barrier at the inner jerrican wall helps to ensure stiffness.

4 FTIR analysis

The FTIR spectra of jerrican cuttings of the grades A and B showed that immersion tests with E85 at 20 °C and 40 °C only caused an increase in the peak of 1585 cm\(^{-1}\) (C=C stretching vibrations) in the chemical structure of HDPE. These stretching vibrations were caused by the molecular chains breaking due to the exposure to E85. The FTIR spectra of jerrican cuttings of the grades A and B showed that immersion tests with biodiesel at 20 °C and 40 °C led to a broadening of the C=O peak of 1740 cm\(^{-1}\) and the appearance of the hydroxyl group at 3500 cm\(^{-1}\). Both features are explained by secondary degradation products of the polyethylene decomposition process caused by the temperature and unsaturated fatty acid content in the biodiesel since biodiesel decomposes quickly at elevated temperatures. The broadening of the C=O peak to 1740 cm\(^{-1}\) can be attributed to aldehyde carbonyl and ester carbonyl groups mutually overlapping (see the mapping spectra of grade B in Figure 8).

![Figure 9: FTIR-spectra of HDPE grade B after immersion for 12 months in biodiesel at 40 °C](image)

4 Conclusions

4.1 Exposure tests with E10

The results of the measurements of MFR and tensile properties led to the conclusion that packagings made of HDPE grades are suitable for the transport of E10. A permeation barrier, e.g. consisting of polyamide on the inner wall of the packagings, is recommended.

4.2 Exposure tests with E85

It can be stated that measurements of the MFR and tensile properties of the two polyethylene grades after 14 months of exposure to E85 at 20 °C and 40 °C showed no serous damaging influence by fuel with 85% ethanol on the properties of the grades.
4.3 Exposure tests with biodiesel

Biodiesel itself is subject to an ageing process by the formation of unsaturated fatty acids which accelerate the oxidative degradation of polyethylene. This is in accordance with the literature and was confirmed by the FTIR analysis. The FTIR spectra of polyethylene showed that immersion tests with biodiesel at 20 °C and 40 °C caused a broadening of the C=O peak of 1740 cm⁻¹ and the appearance of the hydroxyl group at 3500 cm⁻¹ due to the formation of unsaturated fatty acids. The measurements of MFR and tensile Properties lead to the conclusion that polyethylene grades are not suitable for long-term contact with biodiesel.

4.4 Exposure tests with B10

B10 contains 10% biodiesel. The MFR increase of 43% at 20 °C and 44% at 40 °C after three years of exposure was high. A lower decrease in the tensile properties was visible due to the influence of the permeation barrier. Such a fluorinated permeation barrier on the inner jerrican wall helps to ensure the stiffness of the jerricans. Therefore, we recommend the use of packagings with a permeation barrier for the transport of B10.

5 References