

Compatibility of polymers exposed to heating oil blends with 10 % and 20 % biodiesel (FAME)

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ABSTRACT

Biodiesel (FAME) from rapeseed is an environmentally friendly alternative to common fossil fuels. It is also suitable to serve as blending component to fuels like heating oil. If the fuel composition is changed, materials compatibility must be guaranteed. Adding polar biodiesel to nonpolar heating oil, changes the blend's solvency and might cause swelling, extraction and solvation of polymers.

The objective of this research was to investigate the compatibility of polymeric materials, which are commonly used for components in middle distillate facilities, along with blends of heating oil and 20 % biodiesel (B20). For this propose, ACM, HNBR, FKM, PE, PA 6, POM, PUR and PVC were exposed to heating oil and B20 for 42 and 84 days at 40 °C. In addition, the polymers HNBR, FKM, PA, POM and PVC were also exposed at 70 °C. Furthermore, the resistance of polymers in eight-year aged B10 at 40 °C was evaluated. Ageing of biodiesel increases acidity which might propagate polymer corrosion.

The materials were evaluated as resistant, if the loss in tensile properties (tensile strength and elongation at break) and Shore hardness remained under 15 % compared to the initial unexposed material values. For investigations under compressed conditions, the compression set was determined for specimens of ACM, FKM and HNBR after exposure in heating oil B0 and B20 for 3,7,14, 28, 56 and 90 days at 40 °C according to ISO 815-1.

It was found that the resistance in B20 at 40 °C was given for all tested polymers except PUR. In the 8 years aged B10, PUR and POM were not compatible and ACM just conditionally compatible. At 70 °C, FKM and PVC were resistant in B20, whereas HNBR and PA 6 were not compatible. Swelling occurred for the elastomers ACM, HNBR and PUR.

Key words: Biodiesel, FAME, RME, polymers in fuels

INTRODUCTION

Biodiesel (Fatty Acid Methyl Ester, FAME) is gained from renewable resources like rapeseed (RME) and is an essential energy source. It can be blended with common fossil fuels like heating oil and in regions without natural fossil oil deposits Biodiesel is also able to mitigate a dependence on external oil supplies. Therefore, it is desirable to increase the amount of biodiesel made from rapeseed as blending component. At the same time, materials compatibility must be guaranteed whenever changing fuel composition. The question arises if polymeric materials are resistant to heating oil with up to 20 % RME. Addition of polar biodiesel to nonpolar heating oil changes the blend's solvency and might cause swelling, extraction and solvation of polymers and change their physical properties.¹ Furthermore, extracted constituents of polymers alter the fuel chemistry and the unsaturated fatty acids of biodiesel are prone to oxidation.² This can lead to accelerated ageing of the fuel itself followed by degradation of the polymers by enhanced hydrolysis and oxidation which strengthens the loss of stabilizers and additives.³ Hence, cross-linking and chain scission of polymers occur, which cause embrittlement and changes in mechanical properties like hardness, strength, elongation and compression set.^{4,5}

The objective of this research was to determine the resistance of polymers frequently used for components in middle distillate facilities, such as ACM, FKM, HNBR, PA, PE, POM, PUR and PVC in heating oil and a blend of heating oil and 20 % biodiesel (B20). In addition, the compatibility of the polymers in 8-years aged blend of heating oil and 10 % biodiesel (B10) was investigated. The polymers were exposed to the fuels for 42 and 84 days at 40 °C. HNBR, FKM, PA, POM, PUR and PVC were additionally tested at a higher temperature at 70 °C. The material parameters mass, tensile strength, breaking elongation and Shore hardness were determined.

EXPERIMENTAL PROCEDURE

Selection of test materials and test fuels

Table 1 lists the used fuels and some of their properties. The investigated polymers are frequently utilized in middle distillate facilities for components like tanks, sealings and piping (Table 2).

Table 1
Test Fuels

		Oxidation stability (PetroOxy) min	Water content mg/kg	Acidity number -
B0	Heating oil	240	58	< 0.02
B20	Heating oil + 20 % FAME (RME 1)	75	80	0.01
B10, 8 years old	heating oil + 10 % FAME (RME 2)	64	205	2.49

Table 2
Tested Polymers

ACM	Acrylic rubber
HNBR	Hydrogenated nitrile butadiene rubber
FKM	Fluorinated rubber
PUR	Polyurethane rubber
PA 6	Polyamide 6
PE	Polyethylene
POM	Polyoxymethylene
PVC	Polyvinyl chloride

Preparation of test specimens

The specimens were punched from plates of around 2 mm and 3 mm thickness. The specimens for tensile testing of PVC and POM were waterjet-cut because of their brittleness. The dog-bone shaped specimens have a total length of 110 mm and a 4 mm broad web according to EN ISO 527, type 5A⁶. The round specimens for hardness testing have a diameter of 35 mm. For each exposure test three specimens of hardness and five specimens for tensile testing were used.

Determination of change in mass and visual detection

After exposure, the specimens were rinsed and cleaned by a paper towel. The weight was determined using an analytical laboratory scale having a 10⁻⁴ g accuracy before and after exposure within the fuels at the standard laboratory temperature of 23 °C. After exposure the test specimens were inspected visually to detect damage such as greater swelling and volume change.

Exposure tests in fuels

The specimens were attached to a sample holder by a PTFE rod. They were vertically completely immersed in the fuels. After closing the jars⁷ with a sufficiently tight-fitting lid the specimens for hardness and tensile testing were stored in a climate cabinet at 40 °C for 6 weeks and 12 weeks, respectively.

Determination of tensile properties

The tensile properties: tensile strength and breaking elongation were determined according to DIN 53504⁸ immediately after exposure at the standard laboratory temperature of 23 °C. Tensile testing was performed at a constant speed by a Zwick Roell Z005.[†]

Determination of Shore hardness

The Shore hardness A was measured for the elastomers and for the harder polymers the Shore hardness D according to DIN ISO 7619-1 at the standard laboratory temperature of 23 °C.⁹

[†] Trade name

For investigations under compressed conditions, the mass and the compression set of ACM, HNBR and FKM was determined before and after exposure for 3, 7, 14, 28, 56 and 90 days in B20 at 40 °C according to ISO 815-1.¹⁰ Three round rubber test pieces were compressed in a clamping device with steel spacers and put in jar with the fuel. After exposure the thickness was measured at regular intervals over a longer period and based on this, the compression set (%) was calculated by

$$\frac{h_0 - h_1}{h_0 - h_s} \cdot 100, \text{ where} \quad (1)$$

h_0 ... initial thickness of specimen (mm)

h_1 ... thickness of specimen after recovery (mm)

h_s ... height of spacer (4.7 mm).

RESULTS

In the international standards for such applications there are no acceptance criteria determined for the reduction in tensile properties and Shore hardness. Therefore, a threshold of 15 % was set for the evaluation. If the change in tensile properties and Shore hardness remained under 30 %, the polymer is regarded as conditionally resistant in the media, depending on the scope of application.

Change in mass, swelling and appearance

Swelling occurred for the elastomers ACM, HNBR and PUR as shown in Figure 5.

After 84 days at 40 °C, the mass change was almost the same in B0 and B20, except for PUR, where B20 caused a slightly higher fuel adsorption. No or only tiny mass changes occurred for FKM, PA 6, POM and PVC. The eight years old B10 caused significantly stronger swelling of ACM, HNBR and PUR than the other fuels (Figure 1, Figure 2).

At 70 °C, swelling arose for HNBR in B0 and B20; the mass increase in B20 (+42 %) was more than three times as high as in B0 (+13 %) after 84 days exposure (Figure 6). In contrast, the elevated temperature did not increase the mass uptake in B0. No or just tiny mass increase (up to 2 %) occurred for FKM, PUR and POM in B0 and B20.

The fuels caused dark patterning of PE (Figure 4) and the exposure at 70 °C caused yellowing of PA 6 (Figure 3).



Figure 1: PUR after 84 days exposure at 40 °C, from left to right: reference, without media, B0, B20 and aged B10