



## Degradation of carbon-black-filled acrylonitrile butadiene rubber in alternative fuels: Transesterified and hydrotreated vegetable oils



S. Akhlaghi<sup>a</sup>, A.M. Pourrahimi<sup>a</sup>, M.S. Hedenqvist<sup>a</sup>, C. Sjöstedt<sup>b</sup>, M. Bellander<sup>b</sup>, U.W. Gedde<sup>a,\*</sup>

<sup>a</sup> KTH Royal Institute of Technology, School of Chemical Science and Engineering, Fibre and Polymer Technology, SE-100 44 Stockholm, Sweden

<sup>b</sup> Engine Performance and Emissions, Materials Technology, UTMC, Scania CV AB, SE-151 87 Södertälje, Sweden

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### ABSTRACT

The deterioration of acrylonitrile butadiene rubber (NBR), a common sealing material in automobile fuel systems, when exposed to rapeseed biodiesel and hydrotreated vegetable oil (HVO) was studied. The fuel sorption was hindered in HVO-exposed rubber by the steric constraints of bulky HVO molecules, but it was promoted in biodiesel-exposed rubber by fuel-driven cavitation in the NBR and by the increase in diffusivity of biodiesel after oxidation. The absence of a  $\tan \delta$  peak of the bound rubber and the appearance of carbon black particles devoid of rubber suggested that the cavitation was made possible in biodiesel-aged rubber by the detachment of bound rubber from particle surfaces. The HVO-exposed NBR showed a small decrease in strain-at-break due to the migration of plasticizer from the rubber, and a small increase in the Young's modulus due to oxidative crosslinking. A drastic decrease in extensibility and Payne-effect amplitude of NBR on exposure to biodiesel was explained as being due to the damage caused by biodiesel to the continuous network of bound rubber-carbon black. A decrease in the ZnO crystal size with increasing exposure time suggested that the particles are gradually dissolved in the acidic components of oxidized biodiesel. The  $Zn^{2+}$  cations released from the dissolution of ZnO particles in biodiesel promoted the hydrolysis of the nitrile groups of NBR.

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### 1. Introduction

Concerns over the environmental impacts of petroleum-based fuels and shrinking reserves of fossil fuels have led to a global effort to develop alternative fuels that promise more sustainable development and renewability. Biodiesel is currently in focus as a mature biofuel with a broad availability of renewable feedstock and an expanded infrastructure, suitable for conventional engines [1]. Biodiesel fulfils automotive standards and is a clean-burning fuel [2]. However, the deteriorative effect of biodiesel on conventional automotive parts has not been free of controversy. The damage caused by biodiesel to rubber O-rings, seals and hoses in the fuel system causes severe running problems such as fuel filter plugging, fuel leakage and fuel pump failure [3,4].

Biodiesel is produced by the transesterification of vegetable oils to fatty acid methyl esters, but the allylic and *bis*-allylic protons of

unsaturated fatty acid methyl esters of biodiesel are susceptible to oxidation [5]. Over an extended storage period and at high service temperatures, they readily oxidize to allylic hydroperoxides which are unstable and decompose to corrosive compounds such as aldehydes, ketones, alcohols and carboxylic acids [6,7]. In case of rapeseed biodiesel, the hydroperoxides and acidic compounds are formed after only 7 days at 90 °C [8]; and it takes no longer for acrylonitrile butadiene rubber (NBR) to absorb 20 wt.% of biodiesel at the same temperature [8]. The uptake of fatty acid methyl esters and their oxidation products results in a deterioration of the rubber by the extraction of additives such as plasticizer and stabilizer from the rubber and by promoting oxidation of the rubber [8].

The degradation of carbon-black-filled rubbers in biodiesel is more complicated. A gradual increase in the swelling equilibrium and a drastic decrease in the strain-at-break of carbon-black-filled NBR were reported as being due to the biodiesel-induced internal cavitation in the rubber [8]. Despite the recognition of this phenomenon, the true mechanism of formation of cavities in biodiesel-exposed rubbers is still unknown, and further investigations are needed to clarify the effect of biodiesel on rubber-carbon black

\* Corresponding author.

E-mail address: [gedde@kth.se](mailto:gedde@kth.se) (U.W. Gedde).

interfaces. Besides the rubber-particle interactions, the carbon black reinforcement is affected by the network of particles made up of fibrous elements of carbon black interconnected by rubber bridging chains. The fundamental question is whether the biodiesel attack causes the disruption of the continuous network of carbon black particles or whether it causes only the detachment of the rubber layer from the particle surfaces. In this study, the same rubber as that used by Akhlaghi et al. [8] was exposed to biodiesel but at a lower temperature (80 °C) and for a longer time (166 days). The biodiesel sorption was slowed down in order to make it possible to study the biodiesel-driven structural changes in the rubber in more detail. Special attention was given to the degradation of the rubber chains physically and chemically sorbed on carbon black surfaces, i.e. bound rubber. The possible corrosive effect of biodiesel on zinc oxide particles, commonly added to rubbers as an activator of sulphur vulcanization, was also studied.

A suggestion is made to reduce the incompatibility of biodiesel with rubber parts by converting vegetable oils to a more stable fuel with no or less unsaturation than biodiesel. Hydrotreatment is a conversion method that can transform fatty acid triglycerides into saturated hydrocarbons by utilizing existing refinery units. Hydrotreatment of vegetable oils involves (i) hydrogenation of double bonds; (ii) hydrodeoxygenation, i.e. removal of oxygen in the form of water; and (iii) hydrodecarboxylation, which leads to the elimination of carboxyl groups [9] and [10]. The final product, hydrotreated vegetable oil (HVO), is a mixture of *n*- and *iso*-paraffins and is totally free from sulphur and aromatics [11]. HVO can be stored and transported like petroleum diesel, and no precaution regarding auto-oxidation is needed [12]. The ignition, combustion and emission properties of HVO have been reported [13,14]. Despite the advantages of using HVO over biodiesel, the performance of rubbers in HVO has not yet been studied, leaving a gap in the knowledge of the sorption kinetics of HVO in rubbers, the extraction of the rubber additives on exposure to HVO, and the possible structural changes in the rubber on ageing in HVO.

This study therefore, compares the degradation of NBR in HVO with that in rapeseed biodiesel. The rubber samples were aged in the fuels under conditions similar to those prevailing in vehicle fuel systems by using an automated exposure device. Mass and volume changes were determined for the rubbers on exposure to biodiesel and HVO. The Young's modulus and strain-at-break of the aged rubbers were assessed by tensile testing. The bound rubber degradation was assessed by dynamic mechanical analysis (DMA) and scanning electron microscopy. The oxidation of the exposed rubber was assessed by infrared (IR) spectroscopy and crosslink density measurements. The oxidation of biodiesel was studied using proton nuclear magnetic resonance spectroscopy (<sup>1</sup>H NMR) and titration measurements. The effects of biodiesel and HVO on zinc oxide particles were studied by X-ray diffraction (XRD). In the current study, all the exposures were under vacuum, and the fuels were not in contact with oxygen during the exposure. The fuels were only saturated with oxygen at ambient conditions before the exposure. The deterioration of unfilled and carbon-black-filled NBR in biodiesel and HVO at different oxygen levels will be presented in a coming paper.

## 2. Experimental

### 2.1. Materials

Sulphur-cured NBR sheets (2 × 145 × 145 mm) were manufactured by Trelleborg AB, Sweden. According to thermogravimetry, the rubber contained 47 ± 1 wt.% polymer (71.5 wt.% butadiene and 28.5 wt.% acrylonitrile), 37 ± 1 wt.% carbon black, 6 ± 1 wt.% ash after incineration (containing zinc oxide) and 10 ± 1 wt.% low-

molecular weight additives (including 9 ± 1 wt.% plasticizer, tricresyl-phosphate, as revealed by IR spectroscopy; and smaller amounts (0–2 wt.%) of stabilizer, unreacted curing agents and other extractables). Besides the as-received samples, extracted/purified specimens were also exposed to the fuels. The as-received samples (long strips; 2 × 15 × 60 mm) were extracted at 40 ± 1 °C under ultrasonication (Bandelin Sonorex RK 100H, volume = 3 L, ultrasonic peak output = 320 W, frequency = 35 kHz) for 30 min in tetrahydrofuran (THF; ≥99.7 wt.%; VWR International, Sweden). The plasticizer mass was calculated from the TG curve of the extracted samples. The extracted specimens were finally dried at 75 ± 1 °C for 24 h in a vacuum oven (pressure = 20 kPa), and stored at 23 ± 2 °C for a week.

The rapeseed biodiesel was supplied by Preem AB, Sweden. The fuel specifications provided by the supplier were as follows: freezing point = –15.59 to –16.92 °C (EU method A.1); flash point > 101 °C (ASTM D7094); boiling point > 300 °C; density at 23 °C = 860–900 kg m<sup>-3</sup>; viscosity at 40 °C = 3.5–5 × 10<sup>-6</sup> m<sup>2</sup> s<sup>-1</sup> (SS-EN 14214); vapour pressure = 420 Pa (EU Method A.4).

The HVO (NExBTL Renewable Diesel) was supplied by Neste Oil, Finland. The data for the HVO provided by the supplier were as follows: freezing point = <–20 °C (at 1013 hPa; BS4633, method EC A1); initial boiling point = 180 °C (EN ISO 3405); flash point > 61 °C (at 1013 hPa; EN ISO 2719, method EC A9); density at 20 °C = 770–790 kg m<sup>-3</sup> (EN ISO 12185, EC A3); viscosity at 40 °C = 2.6 × 10<sup>-6</sup> m<sup>2</sup> s<sup>-1</sup> (OECD guideline 114). The fuels were stored in dark glass bottles with PTFE-lined caps at 23 °C.

### 2.2. Ageing of NBR in biodiesel and HVO

#### 2.2.1. Exposure vessel and condensation system

Cylindrical glass vessels (flat-bottomed; volume = 2 L) with inner diameters of 120 mm were used for the exposures. The vessels were equipped with five-necked glass heads, and an inlet and an outlet valves at the side-wall for sampling. A condensation system including a Graham condenser and a cold trap immersed in a water and ice bath was mounted on the head. The condensation system was connected to a vacuum pump through the outlet of the cold trap to enable evacuation of the air from the headspace of the vessel, and to accelerate the condensation of the vapours back to the fuel. To keep the set-up sealed during the exposures, the vessel and the head were sealed with silicone grease, and tightened with a metal clamp.

#### 2.2.2. Heating system

The heating system included a magnetic stirrer and heating plates (600 W; RCT basic safety control, IKA, Germany) coupled with an electronic contact thermometer (ETS-D6, IKA, Germany) with an integrated proportional-integral-derivative controller connected to a glass-coated stainless steel temperature sensor (260 mm length; H 66.51, IKA, Germany). The temperature sensor was inserted into the vessel from the head and immersed in the fuel to control the exposure temperature with a precision of ±0.05 °C. The data obtained from the heating system and a pH probe (LR 1000.64; IKA, Germany) were recorded on-line by Labworldsoft software (V. 5.0; IKA, Germany) through a plug-in card (PCI 8.2, IKA, Germany). The vessels were thermally insulated with a 10 mm-thick glass fibre mat.

#### 2.2.3. Oxygen content measurements

The oxygen content in the headspace of the vessel was measured by a headspace gas analyser (PBI CheckMate 9900, Dansensor, Denmark). The amount of dissolved oxygen in the fuel was measured with an oxygen phase fluorimeter (hydrocarbon-resistant; SEOX-PT125-HCR, Spectrecology, FL, USA) with an integrated

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