Polymer Degradation and Stability 136 (2017) 10–19

Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

Degradation of fluoroelastomers in rapeseed biodiesel at different oxygen concentrations

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ARTICLE INFO

Article history:
Received 22 November 2016
Received in revised form
13 December 2016
Accepted 15 December 2016
Available online 18 December 2016

Keywords:
Degradation
Fluoroelastomers
Biodiesel
Chain cleavage
Dehydrofluorination

ABSTRACT

The degradation of fluoroelastomers (FKM) based on different monomers, additives and curing systems was studied after exposure to rapeseed biodiesel at 100 °C and different oxygen partial pressures. The sorption of fuel in the carbon black-filled FKM terpolymer was promoted by the fuel-driven cavitation in the rubber. The bisphenol-cured rubbers swelled more in biodiesel than the peroxide-cured FKM, presumably due to the chain cleavage caused by the attack of biodiesel on the double bonds formed during the bisphenol curing. With any of the selected types of monomer, the FKM rubbers absorbed biodiesel faster and to a greater extent with increasing oxygen partial pressure due to the increase in concentration of the oxidation products of biodiesel. Water-assisted complexation of biodiesel on magnesium oxide and calcium hydroxide particles led to dehydrofluorination of FKM, resulting in an extensive fuel uptake and a decrease in the strain-at-break and the Young's modulus of the rubbers. An increase in the CH_2-concentration determined by infrared spectroscopy, and the appearance of biodiesel flakes in scanning electron micrographs of the extracted rubbers, were explained as being due to the presence of insoluble biodiesel grafted onto FKM on the unsaturated sites resulting from dehydrofluorination. The extensibility of the GFLT-type FKM was the least affected on exposure to biodiesel because this rubber contained less unsaturation and metal oxide/hydroxide particles.

1. Introduction

The increase in transportation and concerns over environmental impacts of petroleum fuels has led to the search for alternative fuels that offer a more sustainable development and less pollutant emissions. Biodiesel appears to hold the key for a renewable energy source to replace reliance on fossil fuels. Biodiesel is produced by the transesterification of vegetable oils and low-cost feedstocks such as frying oils and animal fats [1]. Combustion of biodiesel in regular compression-ignition engines may release less carbon monoxide, less unburned hydrocarbons and less aromatic emissions than petroleum-based diesel [2]. However, the use of biodiesel in conventional fuel systems causes operational problems such as difficulty in starting the engine and unreliable ignition and, on long-term operation, shortens the lifetime of rubber parts in the engine, injector, fuel tank and fuel filter [3–5]. The degradation of rubber O-rings, hoses and seals in biodiesel-fuelled vehicles leads to unexpected running problems such as fuel line leakage, engine choking and fuel pump failure [6].

Biodiesel is more susceptible to oxidation than petroleum diesel. Biodiesel has an oxidative stability index of 0.8–4 h (at 110 °C; according to EN 14112), i.e. the time that elapses before the fuel reaches maximum rate of oxidation, whereas the oxidative stability index of diesel is 40 h (at 110 °C; according to EN 14112) [7]. A hydrogen abstraction from allylic and *bis*-allylic unsaturated fatty acid methyl esters of biodiesel leads to the formation of allylic radicals, which further react with the dissolved oxygen to form hydroperoxides [8]. Aldehydes, ketones, alcohols and carboxylate acids formed by the decomposition of the hydroperoxides promote the degradation of rubber. The oxidation products of biodiesel cause oxidative crosslinking in the rubber by promoting the formation of carbonyl and etheric groups [4,5]. The attack of oxidation products of biodiesel on rubber-filler interfaces detaches the bound rubber from particle surfaces, and disrupts the rubber-filler network [4,5]. Mono-carboxylic acids (e.g. formic, acetic and

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http://dx.doi.org/10.1016/j.polymdegradstab.2016.12.006
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propionic acids) formed by the oxidation of biodiesel cause reduction reactions in the polar components of rubbers [5].

The service life of rubber parts in the engine and fuel delivery system can be as long as many years. In some locations in the fuel system, the rubber parts are also exposed to very high temperatures. Nevertheless, it takes less than 10 days for acrylonitrile butadiene rubber (NBR) to show a 70% decrease in strain-at-break and 60% decrease in Young's modulus on exposure to biodiesel at 80 °C [5]. Sorption of biodiesel in rubbers is promoted by a fuel-driven cavitation in the rubber. A highly filled NBR absorbed 24 wt% biodiesel after two days exposure to biodiesel at 90 °C, and almost all plasticizer was extracted from the rubber during the same period of time [4]. A pronounced decrease in tensile strength has been reported for chloroprene rubber after only 40 days exposure to biodiesel at 25 °C [9]. An acrylic rubber exposed to biodiesel showed a 65% decrease in strain-at-break after 42 days at 40 °C [10]. The performance of ethylene-propylene-diene and silicone rubbers in biodiesel is also poor [9,11].

Since biodiesel creates an almost impossible operating environment for conventional rubbers, specialty elastomers such as fluororubbers (FKM) are used as sealing materials in fuel systems. Various types of FKMs have recently been developed through the design and control of monomer composition, molar mass distribution and polymer chain branching, offering a combination of good resistance to acids and alkalis, stability at high temperatures, and flexibility at low temperatures [12]. However, none of the available FKMs can be considered a reliable rubber in all respects for biodiesel-related applications. Magnesium oxide, calcium hydroxide and zinc oxide are commonly used to scavenge the halides released from the curing of FKM, but oxidation products of biodiesel have the potential to attack these particles [3]; biodiesel is reported to dissolve zinc oxide particles in NBR on prolonged exposure [5]. The products formed by the dissolution of metal oxides and hydroxides in biodiesel cause either further crosslinking or chain cleavage of the rubber [5]. In addition, hydrogen abstraction from the α-hydrogens of the vinylidene fluoride component of FKM promotes dehydrofluorination of the rubber [13].

Nevertheless, the mechanisms of degradation of FKM in biodiesel are still unknown, and further investigations are needed to clarify the possible reactions between the oxidation products of biodiesel and the rubber. New types of FKMs are continuously being developed for servicing in biodiesel engines, but a practical improvement in the resistance of FKMs to biodiesel requires knowledge of the sorption kinetics of biodiesel in FKM and the effects of biodiesel on FKM additives and cure systems. The performance of FKM in biodiesel also depends on the type and composition of the monomers of the rubber. In this study, three common types of FKMs were aged in biodiesel: a bisphenol-cured FKM copolymer and terpolymer and a peroxide-cured GFLT-type FKM (tetrapolymer FKM with low temperature flexibility). Special attention was given to the effect of oxygen concentration on the degradation of FKM in biodiesel. In practice, besides the dissolved oxygen present in biodiesel, the returned fuel that has already been mixed with oxygen in the injector and the high-pressure pump is fed into the fresh biodiesel in the fuel tank. The concentration of oxygen influences the type and concentration of oxidation products of biodiesel as well as the oxidative degradation of FKM.

This study compares the degradation of different types of FKMs having a fluorine content of 66 wt% in rapeseed biodiesel at 100 °C under vacuum and with air purged into the fuel. The uptakes of biodiesel in the different rubber samples were determined by a gravimetric method. The Young's modulus and strain-at-break of the FKM samples were assessed by tensile testing. The oxidation of FKM and the possible reactions between the biodiesel and the rubber were revealed by infrared spectroscopy. The degradation of the bound rubber component was assessed by scanning electron microscopy and dynamic mechanical analysis. The biodiesel that was solidly attached (bonded) to the aged rubbers was studied by thermogravimetry and differential scanning calorimetry. The concentrations of hydroperoxides and acidic components in the biodiesel were measured by titration. The results provide input for the future design of FKM rubbers with improved resistance towards biodiesel.

2. Experimental

2.1. Materials

The FKM copolymer (FKM-co; grade G-7261) containing 60 wt% vinylidene fluoride and 40 wt% hexafluoropropylene, with a glass transition temperature (T_g) of −20 °C and a density (at 25 °C) of 1810 kg m^{-3}, was supplied by Daikin Industries, Japan. The FKM terpolymer (FKM-ter; grade Viton VTR 9033) containing 45 wt% vinylidene fluoride, 30 wt% hexafluoropropylene and 25 wt% tetrafluoroethylene, with a T_g of −14 °C, was supplied by DuPont, USA. GFLT-type FKM (FKM-G; grade PL 458) containing 35 wt% vinylidene fluoride, 30 wt% tetrafluoroethylene, 35 wt% perfluoromethyl vinyl ether and a small amount a cure-site monomer, with a T_g of −24 °C and a density (at 25 °C) of 1830 kg m^{-3}, was supplied by Solvay, Belgium. Fig. 1 shows the repeating units of the different FKMs. Rubber sheets (2 × 145 × 145 mm^3) of bisphenol-cured FKM-co and FKM-ter, and peroxide-cured FKM-G were manufactured by Trelleborg AB, Sweden. According to energy-dispersive X-ray spectroscopy, thermogravimetry and infrared spectroscopy (IR), the FKM-co contained 57 ± 1 wt% polymer, 19 ± 1 wt% barium sulfate, 10 ± 1 wt% calcium hydroxide ($Ca(OH)_2$), 8 ± 1 wt% magnesium oxide (MgO) and 6 ± 1 wt% chromium(III) oxide; the FKM-ter contained 75 ± 1 wt% polymer, 17 ± 1 wt% carbon black (black N550), 4 ± 1 wt% MgO, 2 ± 1 wt% $Ca(OH)_2$ and 2 ± 1 wt% barium sulfate; and the FKM-G contained 75 ± 1 wt% polymer, 24 ± 1 wt% carbon black (black N550) and 1 ± 1 wt% $Ca(OH)_2$.

The rapeseed biodiesel with a freezing point of −16 to −17 °C (EU method A.1), a density of 860–900 kg m^{-3} (at 23 °C), a kinematic viscosity of 3.5–5 × 10^{-6} mm^2 s^{-1} (at 40 °C; SS-EN 14214) and a vapor pressure of 420 Pa (EU Method A.4) was supplied by

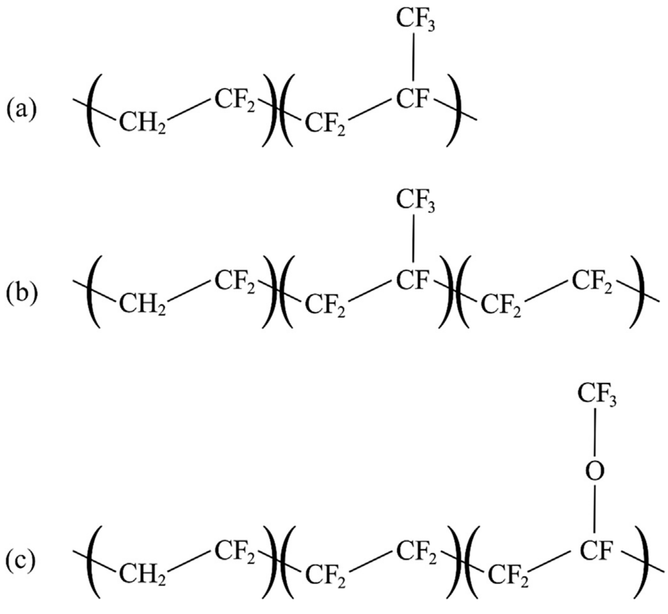

Fig. 1. The repeating units of: (a) FKM-co; (b) FKM-ter; and (c) FKM-G.