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Effects of ageing conditions on degradation of acrylonitrile butadiene rubber filled with heat-treated ZnO star-shaped particles in rapeseed biodiesel

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Abstract

The degradation of acrylonitrile butadiene rubber (NBR) after exposure to biodiesel at different oxygen partial pressures in an automated ageing equipment at 80 °C, and in a high-pressure autoclave at 150 °C was studied. The oxidation of biodiesel was promoted by an increase in oxygen concentration, resulting in a larger uptake of fuel in the rubber due to internal cavitation, a greater decrease in the strain-at-break of NBR due to the coalescence of cavity, and a faster increase in the crosslinking density and carbonyl index due to the promotion of the oxidation of NBR. During the high-temperature autoclave ageing, less fuel was absorbed in the rubber, because the formation of hydroperoxides and acids was impeded. The extensibility of NBR aged in the autoclave decreased only slightly due to the cleavage of rubber chains by the biodiesel attack. The degradation of NBR in the absence of carbon black was explained as being due to oxidative crosslinking. The dissolution of ZnO crystals in the acidic components of biodiesel was retarded by removing the inter-particle porosity and surface defects through heat treating star-shaped ZnO particles. The rubber containing heat-treated ZnO particles swelled less in biodiesel than a NBR filled with commercial ZnO nanoparticles, and showed a smaller decrease in the strain-at-break and less oxidative crosslinking.

Keywords: Acrylonitrile butadiene rubber; Biodiesel; Degradation; Oxidation; Heat treatment; Zinc oxide

1. Introduction

Global effort to reduce reliance on fossil fuels is under way by developing alternative fuels that offer more sustainable development and renewability. The world market for biodiesel, as a renewable fuel, is rapidly growing. Biodiesel consists of fatty acid methyl esters derived from vegetable oils, animal fats and algae [1]. Biodiesel can be produced in petroleum refineries, distributed through existing infrastructure, and combusted in regular diesel engines [2–4]. However, rubber parts have a shorter lifetime in biodiesel-fuelled engines than in engines running with petroleum-based fuels [5–8]. The incompatibility of biodiesel and rubbers has limited the use of biodiesel in a pure form, and has currently led the automotive authorities to recommend using biodiesel in blends with petroleum diesel.

The unexpected failure of rubber O-rings, hoses and seals in automobile fuel systems causes serious running problems, and they are therefore normally guaranteed to have a long lifetime. Nevertheless, a pronounced decrease in the strain-at-break and the Young's modulus has been reported for acrylonitrile butadiene rubber (NBR), a common sealing rubber in fuel systems, after only 10 days' exposure to biodiesel at 90 °C [6]. The rubber exposed to biodiesel became extremely brittle after 40 days, and almost all the plasticizer was extracted from the rubber in the early stages of exposure [6,7]. Carbon-black-filled NBR absorbed up to 110 wt.% biodiesel after 150 days at 80 °C [7]; the swelling equilibrium of the rubber gradually increased due to a biodiesel-driven internal cavitation in the rubber [6–8]. The oxidative crosslinking after the migration of stabilizer from the rubber to the biodiesel causes an increase in the Young's modulus and the glass transition temperature of NBR on prolonged exposure [6–8].

The deteriorative effect of biodiesel on rubbers depends mainly on the concentration of oxidation products in the fuel. Unlike petroleum-based fuels, biodiesel is unstable and readily oxidizes to form corrosive components such as allylic hydroperoxides, aldehydes, ketones, alcohols and carboxylic acids [9]. In rapeseed biodiesel, the hydroperoxide value increased from 150 to 430 mg kg⁻¹ after 30 days at 80 °C [7], and the concentration of acetic acid, formic acid, propionic acid and caproic acid increased exponentially with increasing exposure time [6,7]. The oxidation products of biodiesel tend to accumulate on the large active surface of the carbon black particles [7]. This leads to the disentanglement of the rubber chains

adsorbed on the particles, and the detachment of the bound rubber from the weakest adsorption sites on the particle surface [7]. A decrease in the density of rubber-carbon black junctions leads to the disruption of the rubber-particle network, and a decrease in the extensibility of the rubber [7]. In the present study, an unfilled NBR was exposed to biodiesel in order to investigate the mechanism of degradation of the rubber in the absence of carbon black. Despite fluoroelastomers are currently the preferred materials in fuel systems running in biodiesel, the high cost of fluoroelastomers than NBR has motivated the investigations on the degradation of NBR in biodiesel in order to provide input for the future design of NBR rubbers with improved resistance towards biodiesel.

Zinc oxide (ZnO) particles are commonly used to activate the sulphur curing of rubbers, but biodiesel is reported to diffuse into the inter-particle pores of ZnO agglomerates, and dissolve the particle surfaces [7]. The zinc cations released by the dissolution of ZnO cause reduction reactions in the rubber, and catalyse the oxidation of biodiesel [7]. In an attempt to solve this problem, star-shaped ZnO submicron particles were synthesized by aqueous precipitation as indicated by Pourrahimi et al. [10], and incorporated in the NBR. The inter-particle porosity was eliminated by post-synthesis heat treatment, which is believed to hinder the surface dissolution of the ZnO in the acidic components of biodiesel.

A major gap in the knowledge of the degradation of rubbers in biodiesel is the effects of oxygen concentration on the possible interactions between biodiesel oxidation products and rubbers. Biodiesel dissolves oxygen when exposed to air during storage and transport. For instance, one gram of soybean biodiesel stored in a container with 30 v.% headspace (air) at 25 °C in the dark dissolved 55 µg oxygen [9]. The same type of biodiesel consumed 8.5 ppm dissolved oxygen at a rate of 0.162 ppm h⁻¹ during storage at 55 °C [11]. In practice, fresh biodiesel in the vehicle fuel tank is continuously fed with returned fuel that has already been mixed with oxygen. The oxygen concentration influences the rate and pathway of the oxidation of biodiesel as well as the oxidative degradation of rubbers.

Ageing rubbers in biodiesel at high temperatures under oxygen flushing is not an easy task due to the low flash point of the fuel and safety regulations. Meaningful ageing conditions need to be designed in order to achieve a good relationship between the accelerated ageing and the real service conditions. A specially designed ageing equipment capable of monitoring temperature, oxygen partial pressure in the

headspace and in the fuel, water content and pH of the fuel was used to study ageing of the NBR in biodiesel at 80 and 100 °C and at different oxygen partial pressures. Nitrogen/oxygen gas mixtures were fed into the equipment to adjust the oxygen concentration in the fuel. The highest operating temperature allowed for the equipment was 100 °C (limited by the flash point of biodiesel). Above this temperature, the fuel exposures were performed in an autoclave designed by Scania CV AB, Sweden for gaseous fuel pressures up to 2000 kPa. Variations in headspace volume, oxygen leakage and free access to surrounding oxygen, pressure build up and drawdown and dissimilar fuel hydrodynamics in different exposure devices affect the degradation mechanism of the rubber in biodiesel. In the present study, NBR was aged in the automated equipment and in the autoclave, commonly used for ageing rubbers in fuels at elevated temperatures, to investigate the effect of ageing conditions on the degradation of the rubber in biodiesel.

This study reports on the degradation of a carbon-black-filled NBR exposed to rapeseed biodiesel at 80 °C and oxygen partial pressures (p_{O_2}) of 0, 21 and 40 kPa in the automated ageing equipment, and at 150 °C with a p_{O_2} of 0 kPa in the autoclave. An unfilled NBR was exposed to biodiesel at 80 °C and p_{O_2} of 0 kPa. The degradation of a NBR containing commercial ZnO nanoparticles in biodiesel at 100 °C and $p_{O_2} = 21$ kPa was also compared to that of a NBR containing modified ZnO submicron particles. The concentration of hydroperoxides and acidic components and the fatty acid methyl ester composition of biodiesel were assessed by ^1H NMR and titration methods. The sorption of biodiesel in the rubber samples was determined by a gravimetric method. The Young's modulus and strain-at-break of the NBR samples were assessed by tensile testing. The oxidative reactions of the rubbers exposed to biodiesel were studied by infrared spectroscopy. The glass transition temperature of the samples was determined by differential scanning calorimetry. The synthesis characteristics of the ZnO particles were assessed by scanning electron microscopy, transmission electron microscopy and the Brunauer-Emmett-Teller method. The dissolution of ZnO in biodiesel was studied by X-ray diffraction.

2. Experimental

2.1. Materials

Sheets of sulphur-cured NBR (28.5 wt.% acrylonitrile and 71.5 wt.% butadiene) with a T_g of $-31\text{ }^{\circ}\text{C}$ were manufactured by Trelleborg AB, Sweden. According to thermogravimetry, the rubbers contained 47 ± 1 wt.% polymer, 10 ± 1 wt.% low-molecular weight additives (including 9 ± 1 wt.% oligomeric ether-thioether plasticizer, as revealed by infrared spectroscopy, and a small amount of unreacted sulphur), 37 ± 1 wt.% carbon black (black N990 and black N550, as revealed by scanning electron microscopy) and 6 ± 1 wt.% residual ash including zinc oxide, as revealed by energy-dispersive X-ray spectroscopy. Some of the specimens were extracted before ageing: rubber strips ($2 \times 15 \times 60\text{ (mm)}^3$) were extracted at $40 \pm 1\text{ }^{\circ}\text{C}$ 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 extracted specimens were finally dried at $75 \pm 1\text{ }^{\circ}\text{C}$ for 24 h in a vacuum oven (pressure = 20 kPa), and stored at $23 \pm 2\text{ }^{\circ}\text{C}$ for at least a week. The plasticizer concentration in the extracted samples was determined by thermogravimetry.

Commercial ZnO nanoparticles (ZnO-NanoTek) were supplied by Alfa Aesar, Germany. Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; ≥ 98 wt.%, Sigma Aldrich) and sodium hydroxide (≥ 98 wt.%; Sigma Aldrich) were used as received. High resistivity Milli-Q water ($18.2\text{ M}\Omega\text{ cm}$ at $25\text{ }^{\circ}\text{C}$) was used in the aqueous reaction. The ZnO star-shaped particles were prepared by an aqueous precipitation method described by Pourrahimi et al. [10]: (i) 1 L NaOH aqueous solution (0.5 M) was added to 1 L zinc nitrate hexahydrate aqueous solution (0.2 M) at $60\text{ }^{\circ}\text{C}$ under vigorous stirring for 1h; (ii) the ZnO particles were purified three times in Milli-Q water under ultrasonication (Bandelin Sonorex RK 100H, volume = 3 L, ultrasonic peak output = 320 W, frequency = 35 kHz), dried at $80\text{ }^{\circ}\text{C}$ and normal pressure, ground to a fine powder, and finally dried at $60\text{ }^{\circ}\text{C}$ for 2 h in a vacuum oven (pressure = 20 kPa); and (iii) the ZnO particles were then heated from $23\text{ }^{\circ}\text{C}$ to $600\text{ }^{\circ}\text{C}$ at a rate of $10\text{ }^{\circ}\text{C min}^{-1}$ in ambient air in a muffle furnace (ML Furnaces), kept at this temperature for 1 h, and then cooled to $23\text{ }^{\circ}\text{C}$. Table 1 shows the characteristics of the commercial ZnO nanoparticles and the synthesized particles before and after post-synthesis heat treatment.

Table 1

Sheets of NBR (31 wt.% acrylonitrile and 69 wt.% butadiene; $T_g = -24\text{ }^{\circ}\text{C}$) containing the ZnO nanoparticles and the heat-treated ZnO particles were manufactured by Trelleborg AB, Sweden. The compositions of the NBR samples used in this study were identical.

The rapeseed biodiesel with a flash point of $110\text{ }^{\circ}\text{C}$ (ASTM D7094), an initial boiling point of $300\text{ }^{\circ}\text{C}$ (ASTM E 537-02) and a vapour pressure of 4.2 kPa (EU Method A.4) was supplied by Preem AB, Sweden. The fuels were stored in nitrogen-flushed dark glass containers with PTFE-lined heads at $23\text{ }^{\circ}\text{C}$.

2.2. Ageing devices

2.2.1. Automated ageing equipment

Fig. 1 shows the elements of the ageing equipment used for biodiesel exposure below $100\text{ }^{\circ}\text{C}$ at different oxygen partial pressures. The fuel was pumped into an air-evacuated glass vessel (2 L; inner diameter = 120 mm) with a five-necked head through an inlet valve. The vessel was coupled with a condenser and a cold trap from the head, and covered with an element jacket and thick glass fibre mat for thermal insulation and light protection. The head and the vessel were air-tight sealed with silicone grease (Dow Corning high vacuum grease) and a metal clamp. The equipment was heated on a heating plate (600 W; RCT basic safety control, IKA, Germany). The fuel temperature was controlled with a precision of $\pm 0.05\text{ }^{\circ}\text{C}$ by a glass-coated stainless steel temperature sensor (H 66.51, IKA, Germany) coupled with an electronic contact thermometer (ETS-D6, IKA, Germany) connected to the heater. A pH probe (LR 1000.64; IKA, Germany) was inserted into the vessel to measure the pH of the biodiesel. The oxygen concentration in the headspace of the vessel was measured by a headspace gas analyser (Checkmate 9900, Dansensor A/S, Denmark). The concentration of dissolved oxygen in the fuel was measured with an oxygen phase fluorimeter (hydrocarbon-resistant; SEOX-PT125-HCR, Spectrecology, FL, USA) connected to a transmitter (NEOFOX-GT, Spectrecology, FL, USA). The temperature, pH and p_{O_2} were recorded during the ageing by Labworldsoft software (V. 5.0; IKA, Germany) through a router connected to the sensors.

Fig.1

2.2.2. High-pressure autoclaves

Cylindrical autoclaves (inner diameter = 100 mm, height = 145 mm, volume = 900 mL) made of stainless steel (grade EN 1.4436) were used for the exposure at 150 °C and $p_{O_2} = 0$ kPa. The autoclaves were equipped with right-angled spring-loaded relief valves (type 10.2; Niezgodka GmbH, Germany) on the head. The pressure vessel and the head were sealed by an O-ring (GFLT-type fluoroelastomer, Trelleborg AB, Sweden), and coupled together with a locking ring. The autoclave was placed in a forced-air-circulation oven (model UFE 700; Memmert, Germany), and coupled with the ventilation tubes through the relief valve by steel wire braided PTFE hoses.

2.3. Ageing NBR in biodiesel

Rubber strips ($2 \times 15 \times 60$ (mm)³) and dumb-bells (type c; ASTM D412-06a) were exposed to biodiesel at 80 ± 0.05 and 100 ± 0.05 °C and at $p_{O_2} = 0$, 21 and 40 kPa in the automated ageing equipment. The specimens were hung from a four-legged stand (stainless steel of grade EN 1.4436; $165 \times 60 \times 60$ (mm)³), and placed inside the vessel. The fuel was stirred at a rate of 1200 rpm by a glass-coated magnetic bar (diameter = 8 mm; IKAFLON glass, IKA, Germany). For exposures at 80 ± 0.05 °C and $p_{O_2} = 0$ kPa, the headspace gas was regularly evacuated from the ageing equipment by a vacuum pump. Nitrogen/oxygen gas mixtures were also purged into the fuel at a rate of 50 mL min⁻¹ through a PTFE tube to study the degradation of NBR at $p_{O_2} = 21$ and 40 kPa and 80 ± 0.05 °C. Unfilled-NBR samples were aged in biodiesel at 80 ± 0.05 °C and $p_{O_2} = 0$ kPa in the automated ageing equipment. The NBR samples containing ZnO nanoparticles and synthesized heat-treated ZnO particles were exposed to biodiesel at 100 ± 1 °C, $p_{O_2} = 21$ kPa and a gas flow rate of 100 mL min⁻¹ in the automated ageing equipment. A higher temperature and vigorous gas flushing was used only to accelerate the fuel oxidation and the rubber degradation.

The rubbers were also exposed to biodiesel in the autoclave at 150 ± 1 °C, the specimens being hung from steel wires. The fuel was not stirred during exposure in the autoclave. No oxygen was purged inside the autoclave during the exposure. The fuel was then oxidized due only to the dissolved oxygen in the biodiesel, and the headspace air. Rubber and fuel samples were taken during the exposure, cooled in liquid nitrogen, and stored in plastic zip bags at -25 °C in the dark prior to further analysis.

2.4. Swelling experiments

The biodiesel uptake and plasticizer loss of the rubber strips were determined at 23 ± 1 °C with a precision of 0.01 mg using a Mettler-Toledo balance equipped with a density kit (MS-DNY-54, Mettler-Toledo, Switzerland). The specimens were quickly washed with acetone, and then blotted lightly with a tissue before being weighed. The relative change in mass ($\Delta m/m_0$) was calculated according to:

$$\frac{\Delta m}{m_0} = \frac{(m_1 - m_0)}{m_0} \quad (1)$$

where m_0 and m_1 are respectively the masses of the specimen in air before and after exposure to biodiesel. The mass change of the rubber was due to both uptake of biodiesel and loss of plasticizer, whereas the mass uptake of the extracted rubber (plasticizer was extracted from the rubber before the exposure) was due only to the uptake of biodiesel. Plasticizer loss of the rubbers exposed to biodiesel was calculated by subtracting the mass change of the extracted specimen from that of the as-received rubber containing plasticizer.

2.5. Thermal analyses

The composition of the rubbers was determined by thermogravimetry (TGA/DSC 1, Mettler-Toledo, Switzerland). The sample (mass = 8 ± 0.5 mg) was placed in a 70 μ L aluminium oxide crucible, purged with nitrogen for 1 min at 25 °C, and heated to 550 °C in nitrogen to determine the plasticizer and polymer contents. To determine the carbon black content, the sample was then cooled to 300 °C maintaining the

nitrogen flow, and finally reheated to 800 °C in oxygen. The scanning rate and the gas flow rate were 10 °C min⁻¹ and 50 mL min⁻¹, respectively.

A Mettler-Toledo DSC 1 was used to determine the glass transition temperature of the virgin rubbers. The 7 ± 0.5 mg samples were placed in crimp-sealed 40 µL aluminium pans with a hole in the cover pans, cooled to -80 °C, kept at this temperature for 5 min, and then heated to 150 °C in nitrogen. The scanning rate and the gas flow rate were 5 °C min⁻¹ and 50 mL min⁻¹, respectively. Before the measurements, the soluble species was extracted from the samples under ultrasonication at 40 ± 0.1 °C for 30 min in *n*-hexane (≥ 99 wt.%; AnalaR NORMAPUR, VWR International, Sweden), 30 min in acetone (≥ 99.8 wt.%; AnalaR NORMAPUR, VWR International, Sweden), and 30 min in THF. The extracted samples were dried for 24 h at 70 ± 1 °C under reduced pressure (20 kPa).

2.6. Tensile testing

The dumb-bell-shaped specimens, 115 mm long and 2 mm thick, were cut from the rubber sheets in an Elastocon pneumatic cutting press, EP 02. Tensile tests were performed at 25 ± 1 °C and 50 ± 5 % RH in an Instron 5944 Universal Tensile Testing Machine using a 500 N load cell according to ASTM D412-06a. The crosshead speed and gauge length were 500 mm min⁻¹ and 30 mm, respectively. The average strain-at-break and Young's modulus (secant modulus at 5 % strain) were determined for four specimens of each sample.

2.7. Scanning electron microscopy

Cross-sections of the fresh and aged NBR samples (fractured in liquid nitrogen) and the morphology of the ZnO particles were studied using a field emission scanning electron microscope (Hitachi S-4800). The rubber and powder samples were coated for 20–30 s with a thin conductive layer of Pt/Pd (60/40) using a current of 80 mA in a Cressington sputter coater, model 208 HR. The micrographs were taken at an acceleration voltage of 5 kV and a current of 10 µA.

2.8. Transmission electron microscopy

The commercial ZnO nanoparticles from an ultrasonicated suspension of ethanol (particle concentration = 0.45 ± 0.05 g L⁻¹) were deposited on 400 mesh copper grids

with an ultrathin holey/lacey carbon film (Ted Pella, USA). The prepared samples were then dried, and examined in a transmission electron microscope (Hitachi HT7700) at 100 kV acceleration voltage.

2.9. The Brunauer-Emmett-Teller method

The specific surface area and pore size distribution of the ZnO particles were determined by the Brunauer-Emmett-Teller (BET) method based on nitrogen adsorption/desorption with a Micromeritics ASAP 2000 at 77 K. Before the measurements, the samples were degassed at 200 °C until the pressure reached 0.3 hPa.

2.10. Infrared spectroscopy

The oxidation of the NBR samples was monitored by infrared spectroscopy in a Perkin-Elmer FT-IR Spectrometer 2000 equipped with an attenuated total reflectance accessory (Graseby Specac Ltd, UK). The samples were extracted in THF, acetone and *n*-hexane before the IR measurements according to Section 2.5. The concentration of biodiesel in the extracted rubber was determined by thermogravimetry.

2.11. Crosslink density measurement

The crosslink density of the rubber samples was determined using the Flory-Rehner equation according to ASTM D6814-02. The samples were first extracted according to the method described in Section 2.5, and then dried for 24 h at 70 ± 1 °C under reduced pressure (20 KPa). The dried samples were immersed in benzene (EMSURE® ACS, Merck Millipore, Germany) for 72 h at 23 ± 1 °C. The solvent was refreshed every 24 h. The swollen samples were weighed before and after drying at 70 ± 1 °C for 19 h. The effective number of chains in a real network per unit volume (v_e) was calculated [12] according to:

$$v_e = \frac{-[\ln(1-V_r) + V_r + \chi V_r^2]}{\left[\frac{V_s (\sqrt[3]{V_r} - V_r)}{2} \right]} \quad (2)$$

where χ and V_s are respectively the polymer-solvent interaction parameter ($\chi = 0.486$ [13]) and the molecular volume of solvent, and V_r is volume fraction of the polymer in the swollen network, calculated [12] according to:

$$V_r = \frac{\frac{W_r}{\rho_r}}{\frac{W_r}{\rho_r} + \frac{W_s}{\rho_s}} \quad (3)$$

where W_r , W_s , ρ_r and ρ_s are respectively the mass of dried rubber, the mass of solvent absorbed by the sample, the density of dried rubber and the density of solvent. The crosslink density values were corrected with respect to the volume fraction of the fillers.

2.12. Dynamical mechanical analysis

Strain-sweep tests were carried out on the rubber samples by a Q800 DMA analyzer (TA Instruments, USA) in the tensile mode. The rubber samples ($2 \times 10 \pm 1 \times 50 \pm 1$ (mm)³) were fixed between the clamps with a gauge length of 20 mm, and the storage and loss moduli of the samples were recorded at 80 °C over strains ranging from 0.1 to 20 %. The rubbery state of the samples was determined by temperature-sweep tests. The samples were cooled to -120 °C, kept at this temperature for 5 min, and then heated to 150 °C at a rate of 10 °C min⁻¹ and a constant frequency of 1 Hz.

2.13. Wide-angle X-ray diffraction

X-ray diffractograms of the rubber samples were taken at 25 ± 0.1 °C using a PANalytical X'pert Pro MPD diffractometer with Cu-K α radiation (wavelength = 1.54 Å) at a current of 45 mA and a generator voltage of 45 kV. The data were collected between 5 and 40° (2 θ) at a scanning step time of 10.16 s and a step size of 0.004° (2 θ).

2.14. Determinations of the hydroperoxide value, acid value and the fatty acid methyl ester composition of biodiesel

The hydroperoxide value of the biodiesel samples was determined according to ASTM D3703-13. The concentration of acidic components of biodiesel aliquots was measured according to ASTM D974-12. The method used to measure hydroperoxide and acid values has been reported by Akhlaghi et al. [6]. The content of the fatty acid methyl esters of the biodiesel samples was determined by a ^1H NMR spectrometer (Bruker Avance 400 MHz, Billerica, MA, USA), according to the method described by Akhlaghi et al. [6]. The samples were dissolved in chloroform-*d* (99.96 % atom D containing 0.03 v.% trimethylsilane; Sigma-Aldrich, Sweden) in a 5-mm NMR tube. The measurements were performed at 25 ± 1 °C, a spectral width of 10 kHz, a chemical shift of $\delta = 0\text{--}12$ ppm and a FID 90° pulse length of 8.55 μs . MestReNova software was used to analyse the data.

3. Results and discussion

3.1. Degradation of carbon-black-filled NBR in biodiesel at different oxygen concentrations

3.1.1. Oxidation of biodiesel at 80 °C and different oxygen partial pressures

Figs. 2a-c show the relative changes in the concentrations of unsaturated fatty acid methyl esters (u-FAME), hydroperoxides and acids in biodiesel at 80 °C and $p_{\text{O}_2} = 0, 21$ and 40 kPa as functions of exposure time. At any of the selected oxygen activities, the concentration of u-FAMEs decreased with increasing exposure time (Fig. 2a). As the oxygen concentration increased, u-FAMEs of biodiesel oxidized more rapidly and to a greater extent. The oxidation products of u-FAMEs, hydroperoxides, were rapidly formed in the early stages of the exposure (Fig. 2b). Under vacuum, the concentration of hydroperoxides increased with increasing exposure time, and then remained constant after 34 days. During the first 7 days, a larger amount of hydroperoxides was formed in the fuel on aerobic than on anaerobic exposure. After 7–10 days at $p_{\text{O}_2} = 21$ and 40 kPa, the rate of decomposition of hydroperoxides exceeded the formation rate, and thus the hydroperoxide value decreased. The decomposition of the hydroperoxides levelled off after 41 days at

$p_{O_2} = 21$ kPa, whereas almost all hydroperoxides formed during the initial stages of the exposure were consumed after 83 days at $p_{O_2} = 40$ kPa (Fig. 2b). The concentration of acidic components of biodiesel significantly increased with increasing exposure time (Fig. 2c). A higher oxygen concentration promoted the formation of acids in the biodiesel. The initial rate of the decrease in the concentration of u-FAMEs and the increase in the acid value of the biodiesel had a linear relationship with the p_{O_2} (see the inset images in Figs. 2a and c).

Figs. 2a-c

3.1.2. Effect of oxygen partial pressure on the swelling of carbon-black-filled NBR in biodiesel at 80 °C

Fig. 3a shows the uptake of biodiesel and loss of plasticizer of carbon-black-filled-NBR at 80 °C and $p_{O_2} = 0, 21$ and 40 kPa as a function of exposure time. On both aerobic and anaerobic exposure, a large amount of biodiesel was initially absorbed by the rubber after 17 h (regime I in Fig. 3a; see inset curves in Fig. 3a). The uptake of biodiesel in NBR at $p_{O_2} = 0$ and 21 kPa then increased linearly until equilibrium was reached at $\Delta m/m_0 \sim 120$ %. The mass of NBR was equilibrated after 150 days at $p_{O_2} = 0$ kPa, and after 80 days at $p_{O_2} = 21$ kPa. At $p_{O_2} = 40$ kPa, the sorption curve of NBR showed two different kinetics regimes after day 1: (i) a fast linear increase in mass with increasing exposure time that was completed after 50 days, followed by (ii) a slow linear increase in the uptake of biodiesel as a function of exposure time that never ended during the exposure period of 154 days. Fig. 3b shows the linear relationship between the initial rate of the uptake of biodiesel in the rubber (from day 2 to day 50) with the p_{O_2} .

Figs. 3a and b

The mass of NBR increased more rapidly with increasing p_{O_2} . Plasticizer migration from the rubber was also promoted by increasing oxygen concentration (Fig. 3); all the plasticizer left the rubber after 3 days at $p_{O_2} = 40$ kPa. Akhlaghi et al. [6,7] reported that the oxidation products of biodiesel partially accumulated on the

accessible part of carbon black surfaces, and degraded the bound rubber layer adsorbed on the surface of particles, causing internal cavitation in the rubber. Larger amounts of hydroperoxides and acids were generated by the oxidation of biodiesel on aerobic exposure, which caused more severe damage to the rubber, resulting in a greater and more rapid fuel uptake and plasticizer loss.

3.1.3. Structural changes in carbon-black-filled NBR on exposure to biodiesel at 80 °C and different oxygen concentrations

Fig. 4 shows the strain-at-break (ϵ_b) of carbon-black-filled-NBR exposed to biodiesel at 80 °C and $p_{O_2} = 0, 21$ and 40 kPa, as a function of exposure time. The ϵ_b of the rubber significantly decreased with increasing exposure time, the decrease being more pronounced on aerobic exposure than under vacuum. In Fig. 5 (inset curve), a gradual breakdown of the bound rubber-carbon black network in the fresh NBR, the Payne effect, was evident from a large difference between the storage moduli at very low and relatively high strains ($E'_0 - E'_\infty$) [14]. On exposure to biodiesel, the ($E'_0 - E'_\infty$) value of the rubber decreased with increasing exposure time (Fig. 5), suggesting that the rubber-particle network was damaged by the biodiesel attack. The biodiesel-induced network disruption was promoted by an increase in the p_{O_2} , resulting in a greater decrease in the extensibility of the rubber at $p_{O_2} = 21$ and 40 kPa than at $p_{O_2} = 0$ kPa.

Figs. 4 and 5

The Young's modulus of carbon-black-filled NBR decreased after 10 days' exposure to biodiesel (Fig. 6), due to a great uptake of fuel during this period of time. At longer exposure times, NBR showed an increase in the Young's modulus. The increase in the carbonyl index (the ratio of IR absorbance of the carbonyl groups at 1758 cm^{-1} to the CH_2 groups at 2944 cm^{-1} ; Fig. 7a), and the increase in crosslinking density of NBR with increasing exposure time (Fig. 7b) indicated that the stiffening of the rubber was caused by oxidative crosslinking.

Figs. 6 and 7

Carbon-black-filled NBR exposed to biodiesel at $p_{O_2} = 40$ kPa showed the greatest increase in carbonyl index and crosslinking density, but the Young's modulus of the aged rubber at $p_{O_2} = 40$ kPa was lower than at $p_{O_2} = 21$ kPa. The extensive biodiesel-driven bound rubber degradation at $p_{O_2} = 40$ kPa caused the cavities surrounding the carbon black particles to grow, and coalesce into larger vacuoles (Figs. 8a and b). The coalescence of the cavities resulted in the uptake of a considerable amount of biodiesel (see Fig. 3), and a decrease in the Young's modulus that compensated for the rubber stiffening caused by oxidative crosslinking. The initial rate of the increase in the carbonyl index of the aged rubber had a linear relationship with the p_{O_2} (see the inset images in Fig. 7a).

Fig. 8

3.2. Degradation of carbon-black-filled NBR in biodiesel at 150 °C: ageing conditions on autoclave exposure

3.2.1. Oxidation of biodiesel on autoclave exposure at 150 °C

Fig. 9a shows the concentrations of methyl linolenate (C18:3; u-FAME with three double bonds in the backbone), methyl linoleate (C18:2; u-FAME with two double bonds in the backbone) and mono-unsaturated FAMES of biodiesel on autoclave ageing at 150 °C as a function of exposure time. The concentration of C18:2 slightly decreased with increasing exposure time. The mono-unsaturated FAMES and C18:3 showed no significant oxidation activity during the exposure period of 38 days (Fig. 9a). The hydroperoxide value of biodiesel initially decreased at 150 °C (day 3), and then showed a small increase after 7 days (Fig. 9b). All the hydroperoxides were consumed on further oxidation of biodiesel; the hydroperoxide value of biodiesel was almost zero after 38 days (Fig. 9b). The acid value of the biodiesel showed a small increase at 150 °C after 11 days (Fig. 9b). From day 11 and onwards, the concentration of acids remained constant.

Fig. 9

The u-FAME of biodiesel oxidized less on autoclave ageing at 150 °C than on exposure in the automated ageing equipment at 80 °C and $p_{O_2} = 0$ kPa, resulting in the formation of a smaller amount of hydroperoxides and acidic components (cf. Figs. 2a-c and Figs. 9a and b). The initial oxidation reactions of biodiesel lead to the formation of alkyl radicals [15], which normally react with oxygen to form alkylperoxyl radicals which, in turn, abstract a hydrogen from other fatty acid methyl ester molecules, to form hydroperoxides [16]. At 150 °C, when the oxygen partial pressure decreased, the termination reactions such as polymerization and cyclization of alkyl and alkylperoxyl radicals dominated over the reaction of alkyl radicals and oxygen [11], and thus the formation of hydroperoxides and acids was retarded.

As the exposure temperature increased, the hydroperoxides decomposed more rapidly than they were formed [15]. The fast decomposition of the hydroperoxides at the beginning of the autoclave exposure at 150 °C gave a rapid rise in the concentration of acids (Fig. 9b). The fuel was not stirred during the exposure in the autoclave, and thus the oxygen in the headspace air transferred into biodiesel only by diffusion, whereas the headspace oxygen in the automated ageing equipment went into the stirring fuel by both diffusion and convection [15]. The amount of headspace air in the automated ageing equipment was greater than that in the autoclave. When oxygen is abundant, the stabilizers present in biodiesel can hardly react with alkyl radicals; oxygen reacts more rapidly with alkyl radicals (reaction rate constant $\sim 2 - 8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ [11]). On autoclave ageing at 150 °C, the stabilizer molecules were more likely to react with alkyl radicals, and contributed more to inhibiting the oxidation reactions.

3.2.2. Swelling and structural changes in carbon-black-filled NBR exposed to biodiesel at 150 °C in autoclaves

The sorption of biodiesel in carbon-black-filled NBR at 150 °C on autoclave exposure (Fig. 10) showed a two-stage diffusion process: (i) during the first 3 days, NBR absorbed ca. 16 wt.% biodiesel, accounting for 70 % of the total fuel uptake by the rubber after which (ii) the fuel uptake slowly increased until day 7, and then reached equilibrium. The migration of the plasticizer from the rubber was faster at 150 °C than at 80 °C and $p_{O_2} = 0$ kPa (cf. Fig. 3 and Fig. 10); the rubber lost 90 % of

the plasticizer during the first 7 days at 150 °C. The remaining plasticizer was extracted from the rubber after 38 days (Fig. 10).

Fig. 10

Fig. 11 shows the ε_b and Young's modulus of carbon-black-filled NBR exposed to biodiesel at 150 °C in the autoclave. The ε_b of the rubber decreased slightly after 3 days' exposure to biodiesel, probably due to the migration of plasticizer from the rubber. The rubber showed no significant change in the ε_b on further exposure to biodiesel. The Young's modulus of NBR decreased extensively in the early stages of the exposure, and then remained constant after 3 days (Fig. 11). A decrease in the crosslinking density of NBR exposed to biodiesel (Fig. 12) suggested that biodiesel promoted the cleavage and disentanglement of rubber chains at 150 °C, resulting in a decrease in the stiffness of NBR. The rubber-carbon black interface remained intact in the aged rubber, and the carbonyl index of the rubber did not change after prolonged biodiesel exposure at 150 °C (not shown). The probable reason is that, unlike the exposure in the automated ageing equipment at 80 °C and $p_{O_2}=0$ kPa, the rubber aged at 150 °C in the autoclave was in contact with a smaller amount of hydroperoxides and acids generated from the biodiesel; thus the degradation mechanisms driven by the attack of oxidation products of biodiesel on NBR (bound rubber degradation and promotion of oxidation of the rubber) did not occur at 150 °C.

Figs. 11 and 12

3.3. Degradation of unfilled NBR in biodiesel at 80 °C under vacuum

Fig. 13 shows the sorption of biodiesel in unfilled NBR at 80 °C and $p_{O_2}=0$ kPa. The rubber rapidly absorbed 50 wt.% biodiesel after 18 h, which was followed by a slower uptake. Equilibrium was never reached during the exposure period of 155 days. At the same p_{O_2} and exposure temperature, unfilled NBR absorbed a greater amount of biodiesel than the carbon-black-filled NBR: 240 wt.% (after 155 days; unfilled-NBR) and 120 wt.% (after 155 days; NBR containing 37 wt.% carbon black). All the plasticizer left the unfilled rubber after less than 2 h.

Fig. 13

The ε_b of unfilled NBR decreased remarkably during the first 12 days' exposure to biodiesel (Fig. 14). From day 12 and onwards, the ε_b of the rubber gradually decreased with increasing exposure time from ca. 135 % to ca. 30 % (day 50). The unfilled and carbon-black-filled NBR showed an analogous decrease in the ε_b on exposure to biodiesel (cf. Fig. 4 and Fig. 14). However, the increase in the Young's modulus of NBR on prolonged exposure to biodiesel was greater if no carbon black was incorporated in the rubber (cf. Fig. 6 and Fig. 14). The increase in crosslinking density of NBR exposed to biodiesel was more pronounced in the unfilled than in the carbon-black-filled rubber (cf. Fig. 7b and Fig. 15). This suggests that the degradation of unfilled NBR in biodiesel was essentially due to oxidative crosslinking. The oxidation of NBR was essentially promoted by the absorption of a large amount of hydroperoxides and acids produced by the oxidation of the biodiesel.

Figs. 14 and 15

3.4. Dissolution of heat-treated ZnO and commercial ZnO nanoparticles on exposure to biodiesel

Figs. 16a-c show scanning electron micrographs of the commercial ZnO nanoparticles and of the submicron star-shaped ZnO (before and after heat-treatment), used to activate the cure system of NBR. The intra-particle porosity of the star-shaped ZnO particles (Fig. 16b) was eliminated by heat treatment, while the shape of the particles was retained (Fig. 16c). The submicron star-shaped particles showed a complete dispersion and distribution in the rubber, whereas the ZnO nanoparticles formed 10 – 50 μm hard agglomerates (cf. Fig. 17a and Fig. 17b). The same type of ZnO nanoparticles also showed large agglomerates in polyethylene matrix, but the agglomeration was totally disappeared if the particle size increased to a submicron range [17]. The $(M_\infty - M_0)$ value (a difference between the torque value after the end of the cure period (M_∞) and the torque value at the beginning of the curing process (M_0), determined by a moving-disc-rotational rheometer) of NBR containing heat-

treated ZnO particles (21 dN m) was greater than that of the ZnO-nanoparticle-filled rubber (18 dN m). This indicated that the heat-treated ZnO promoted the curing of the rubber. The specific surface area of the ZnO nanoparticles ($33.6 \text{ m}^2 \text{ g}^{-1}$) was greater than that of the synthesized star-shaped particles (see Table 1). After heat-treatment at 600°C , the specific surface area of the synthesized particles decreased from 12.6 to $3.8 \text{ m}^2 \text{ g}^{-1}$ due to the removal of intra-particle pores. Despite the smaller specific surface area of the heat-treated ZnO submicron particles, their “effective” surface area at the rubber-particle interface was larger than the interfacial surface area in the rubber containing agglomerates of the ZnO nanoparticles. The large interfacial surface area of the heat-treated ZnO particles effectively contributed to the curing of the rubber, resulting in a larger ($M_\infty - M_0$) value.

Figs. 16 and 17

Fig. 18 shows the uptake of biodiesel in carbon-black-filled-NBR containing agglomerates of the ZnO nanoparticles and heat-treated star-shaped ZnO at 100°C and $p_{\text{O}_2} = 21 \text{ kPa}$ (gas flow rate of 100 mL min^{-1}). The two NBR samples absorbed the same amount of biodiesel during the first day of the exposure. The uptake of biodiesel in the rubber containing ZnO nanoparticles then increased strongly with increasing exposure time from $\Delta m/m_0 = 17\%$ (day 1) to $\Delta m/m_0 = 90\%$ (day 7); followed by a slow increase in the mass of the rubber up to 28 days. From day 1 and onwards, the mass of the heat-treated-ZnO-filled rubber increased with increasing exposure time at a rate similar to that at the latter stage of the sorption curve of NBR containing agglomerates of the ZnO nanoparticles. However, the NBR swelled significantly less in biodiesel in the presence of heat-treated ZnO ($\Delta m/m_0 = 80\%$; day 28) than when filled with ZnO nanoparticles ($\Delta m/m_0 = 115\%$; day 28).

Fig. 18

On exposure to biodiesel, the heat-treated ZnO-filled rubber showed a smaller decrease in the ε_b than the NBR filled with ZnO nanoparticles (Fig. 19a). The increase in the Young's modulus of the aged rubber due to oxidative crosslinking was more pronounced in the presence of the agglomerates of the ZnO nanoparticles (Fig. 19b). The XRD spectra of the NBR samples show that the characteristic crystalline peaks of

ZnO at 30 – 40° broadened with increasing exposure time, due to a decrease in crystal size caused by a gradual dissolution of the particles in the acidic components of biodiesel (Figs. 20a and b). The ZnO nanoparticles were completely dissolved in biodiesel after 3 days (not shown here), whereas the heat-treated ZnO was still present in the rubber after 7 days' exposure to biodiesel (Fig. 20b). The trace of heat-treated ZnO disappeared in the XRD pattern of the NBR after 13 days (Fig. 20b). Untreated star-shaped ZnO dissolved in biodiesel after 4 days (not shown).

Figs. 19 and 20

The mono-carboxylic acids of biodiesel attack defects on the crystal surfaces of the ZnO particles, resulting in dissolution of ZnO to zinc cations [18]. In case of ZnO nanoparticles, the readily available surface area due to the large pore volume (cumulative pore volume = $0.21 \text{ cm}^3 \text{ g}^{-1}$) promoted the dissolution of the particles in biodiesel. The synthesised star-shaped ZnO particles had a smaller cumulative pore volume ($0.03 \text{ cm}^3 \text{ g}^{-1}$), which further decreased to almost zero after heat treatment. Hence, a smaller part of the non-porous structure of the heat-treated ZnO was accessible to the biodiesel molecules, which hindered the dissolution of bulk ZnO. Heat treatment has been reported to decrease the crystal surface defects due to the relaxation of zinc and oxygen vacancies inside the crystal unit cells of ZnO [17,19]. The removal of the surface defects improved the resistance of ZnO particles towards dissolution in biodiesel.

The zinc cations formed after dissolution of ZnO in biodiesel caused reduction reactions in the nitrile groups of the NBR [7]. The reduced NBR was more vulnerable to biodiesel attack. A rapid dissolution of ZnO nanoparticles in biodiesel led to an extensive fuel uptake by NBR from day 1 to day 7 (see Fig. 18). A consequence of the cavities formed in the rubber due to the dissolution of ZnO was an increase in the fuel uptake by the rubber. Zinc cations also promoted the oxidation of u-FAME of biodiesel absorbed by the rubber [20]. The oxidation products of biodiesel became involved in the oxidative reactions of the rubber, and this led to a significant increase in the Young's modulus of ZnO-nanoparticle-filled NBR (see Fig. 19b). Akhlaghi et al. [8] has reported that the water produced by the oxidation of biodiesel caused the surface complexation of biodiesel on the metal oxide particles. The coordination complexes of biodiesel and ZnO particles may also be formed, and

presumably cause reduction reactions in NBR. The hydroxyl groups on the surface of the star-shaped ZnO particles were completely removed after heat treatment [21]. This suggests that the heat-treated ZnO particles absorbed no water [21], and that the water-assisted complexation of biodiesel on these particles did not occur.

4. Conclusion

The biodiesel-driven degradation of NBR was studied in the presence and absence of carbon black at 80 °C and different oxygen partial pressures in an automated ageing equipment, and at 150 °C in a high-pressure autoclave. A higher concentration of oxygen promoted the formation of oxidation products of biodiesel, resulting in an extensive uptake of biodiesel in the rubber. The decrease in extensibility of the rubber exposed to biodiesel, caused by the coalescence of cavities, was more pronounced with increasing oxygen partial pressure. The tensile properties of the rubber were less affected by biodiesel attack on high-temperature autoclave ageing, due to retardation of the oxidation of biodiesel. The degradation of the unfilled NBR was caused only by oxidative crosslinking. Heat-treated star-shaped ZnO particles were dissolved more slowly and to a smaller extent in biodiesel than ZnO commercial nanoparticles, due to the elimination of inter-particle porosity and surface defects of particles by heat treatment. The heat-treated ZnO particles dispersed better than the ZnO nanoparticles in the rubber, and promoted the curing of NBR. The rubber filled with the heat-treated ZnO particles absorbed less biodiesel than the rubber containing ZnO nanoparticles, and showed a smaller decrease in the strain-at-break on exposure to biodiesel.

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Legends to figures:

Fig. 1. Schematic diagram of the automated ageing equipment. The equipment was used for ageing carbon-black-filled and unfilled NBR in biodiesel at 80 and 100 °C and at $p_{O_2} = 0, 21$ and 40 kPa.

Fig. 2. The concentrations of: (a) u-FAME; (b) hydroperoxides (PV); and (c) acidic components (AV) of biodiesel (the inset graph shows the initial rate of the increase in the concentration of acids in the biodiesel as a function of p_{O_2}), as functions of exposure time at 80 °C and at $p_{O_2} = 0, 21$ and 40 kPa.

Fig. 3. The uptake of biodiesel and plasticizer loss of carbon-black-filled-NBR, as a function of exposure time at 80 °C and $p_{O_2} = 0, 21$ and 40 kPa. The inset curves show the relative changes in mass of NBR at 80 °C and $p_{O_2} = 0, 21$ and 40 kPa during the first 3 days of exposure, and (b) the rate of the uptake of biodiesel in NBR from day 1 to day 50 as a function of p_{O_2} .

Fig. 4. The relative change in strain-at-break of carbon-black-filled-NBR exposed to biodiesel at 80 °C and at $p_{O_2} = 0, 21$ and 40 kPa, as a function of exposure time.

Fig. 5. The $(E'_0 - E'_\infty)$ values of carbon-black-filled-NBR exposed to biodiesel at 80 °C and at $p_{O_2} = 0, 21$ and 40 kPa, plotted as a function of exposure time. The inset curve shows the storage modulus of a fresh carbon-black-filled-NBR, as a function of strain.

Fig. 6. The relative change in Young's modulus of carbon-black-filled-NBR exposed to biodiesel at 80 °C and at $p_{O_2} = 0, 21$ and 40 kPa as a function of exposure time.

Fig. 7. (a) The carbonyl index (the inset graph shows the initial rate of the increase in the carbonyl index of the rubber as a function of p_{O_2}), and (b) the relative change in crosslinking density of carbon-black-filled-NBR on exposure to biodiesel at 80 °C and at $p_{O_2} = 0, 21$ and 40 kPa, as functions of exposure time.

Fig. 8. Scanning electron micrographs of: (a) fresh carbon-black-filled NBR; and (b) carbon-black-filled NBR aged in biodiesel at 80 °C and $p_{O_2} = 40$ kPa for 29 days.

Fig. 9. The concentrations of: (a) u-FAME; and (b) hydroperoxides (PV) and acidic components (AV) of biodiesel aged in the autoclave at 150 °C and $p_{O_2} = 0$ kPa, as functions of exposure time.

Fig. 10. The uptake of biodiesel and the plasticizer loss of carbon-black-filled-NBR exposed to biodiesel in the autoclave at 150 °C and $p_{O_2} = 0$ kPa, as functions of exposure time.

Fig. 11. The relative changes in strain-at-break and Young's modulus of carbon-black-filled-NBR exposed to biodiesel in the autoclave at 150 °C and $p_{O_2} = 0$ kPa, as functions of exposure time.

Fig. 12. The relative change in crosslinking density of carbon-black-filled-NBR exposed to biodiesel in the autoclave at 150 °C and $p_{O_2} = 0$ kPa, as a function of exposure time.

Fig. 13. The uptake of biodiesel in unfilled-NBR, as a function of exposure time at 80 °C and $p_{O_2} = 0$ kPa.

Fig. 14. The relative changes in strain-at-break and Young's modulus of unfilled-NBR exposed to biodiesel at 80 °C and $p_{O_2} = 0$ kPa, as functions of exposure time.

Fig. 15. The relative change in crosslinking density of unfilled-NBR exposed to biodiesel at 80 °C and $p_{O_2} = 0$ kPa, as a function of exposure time.

Fig. 16. Scanning electron micrographs of: (a) commercial ZnO nanoparticles (the inset image is a transmission electron micrograph of commercial ZnO nanoparticles); (b) synthesized star-shaped ZnO submicron particles before heat treatment; and (c) synthesized star-shaped ZnO submicron particles after heat treatment.

Fig. 17. Scanning electron micrographs showing: (a) distribution of heat-treated ZnO particles; and (b) agglomerates of ZnO nanoparticles in the fresh rubber (unaged).

Fig. 18. The relative change in mass of carbon-black-filled NBR containing commercial ZnO nanoparticles and heat-treated star-shaped ZnO on exposure to biodiesel at 100 °C and $p_{O_2} = 21$ kPa (gas flow rate = 100 mL min⁻¹), plotted as functions of time.

Fig. 19. The relative changes in: (a) strain-at-break and (b) the Young's modulus of carbon-black-filled NBR containing commercial ZnO nanoparticles and heat-treated star-shaped ZnO on exposure to biodiesel at 100 °C, $p_{O_2} = 21$ kPa (gas flow rate = 100 mL min⁻¹), as functions of exposure time.

Fig. 20. XRD patterns of: (a) fresh and biodiesel-exposed carbon-black-filled NBR containing commercial ZnO nanoparticles after 1, 2, 7 and 13 days; and (b) fresh and biodiesel-exposed carbon-black-filled NBR containing heat-treated star-shaped ZnO particles after 1, 2, 7 and 13 days. The rubbers were aged in biodiesel at 100 °C, $p_{O_2} = 21$ kPa (gas flow rate = 100 mL min⁻¹).

Table 1. Characteristics of the commercial ZnO nanoparticles and the star-shaped ZnO micron size particles before and after heat treatment.

ZnO particle	Size ^a (nm)	SSA ^b (m ² g ⁻¹)	Pore Size ^c (nm)
Commercial	25 ± 6	33.6	20 (inter-aggregate)
Before heat treatment	555 ± 146	12.6	3.5 (intra-particle)
After heat treatment	524 ± 137	3.8	0

^a Particle size distribution as revealed by scanning electron microscopy.

^b Specific surface area as revealed by the Brunauer-Emmett-Teller evaluation.

^c Corresponding the BJH (Barret-Joyner-Halenda) pore size as revealed by the Brunauer-Emmett-Teller evaluation.