Studies on thermo-oxidative degradation of synthetic rubbers 1-4 and 1-2 polybutadienes

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Abstract:

The production of natural latex is limited, and the related demand for terrestrial transportation has increased. The synthesis of rubber has become necessary and the resulting synthetics' properties must be known. Thermo-oxidative degradation of synthetic rubbers 1,4- and 1,2-polybutadienes caused by heating the compounds at 100°C in the air, was monitored. The volatile compounds released during the degradation were identified using coupled modern physical methods, including NMR, TGA, MS, FTIR, etc.. Thermal gravimetric analysis showed that oxidation occurred for both 1,4 and 1,2-PB. Below 400°C, major functional groups were formed, including peroxides, ketone, aldehyde, ester, etc.. Oxidation was found to start on the methylene (CH_2) carbon of 1,4-PB and on the methylene (CH_2) and methine (CH) carbons of 1,2-PB. The polycyclohexane-like structures were identified resulting from the oxidation of 1,2-PB. Above 400°C, the main resulting compounds were carbon dioxide, carbon monoxide, water, and some hydrocarbons and aromatics. Radical mechanisms for thermo-oxidative degradation of 1,4 and 1,2-PBs were proposed.

Keywords: FTIR, latex, mechanism, MS, NMR, polybutadiene, rubber, TGA, thermo-oxidative degradation.

Classification number: 2.2

Introduction

In contact with oxygen, polybutadienes can be oxidised even at low temperatures (0°C) [1]. Thermo-oxidative degradation of polymers can match the oxidation of the polybutadiene chain as well as the decomposition of oxidized products. Studies of 1,4-polybutadiene have shown that the major oxidised products have been hydroperoxide, cycloperoxide, alcohol, ether, carboxylic acid, ester, aldehyde, carbon dioxide, carbon monoxide, and water [1-5]. The mechanism for the formation of these products has been only proposed from observations of the FTIR spectrum. The polymer used for the studies has a high molecular weight which limited the resolution of analytical technics. For 1,2-polybutadiene, the thermo-oxidative degradation seemed not to be mentioned in previous publications.

In this paper, we aim to use polybutadiene's low molecular weight. The thermo-oxidative degradation of the polybutadiene (PB) with various chemical structures was investigated. The oxidisation process of product formation was monitored by heating the PBs in the air and identifying the corresponding residues using FTIR-ATR and NMR. The volatile compounds released during the degradation were investigated using TGA/FTIR and TGA/TD-GC/MS. Most probable degradation mechanisms were proposed.

Experimental

Materials and sample preparation

Polybutadienes (PBs) were provided by Polymer Laboratories Ltd. The PB samples were synthesised using sec-butyl lithium as an initiator. The structure of the PB samples was characterised using ^{13}C-NMR spectrometry. Average molecular weight was determined by Size Exclusion Chromatography (SEC) combined with a laser scattering detector. The result was summarised in Table 1 [6].

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Table 1. Properties of PBs.

	% 1,2-vinyl[b]	% 1,4-cis[b]	% 1,4-trans[b]	Mn[a]
1,4-PB	8	33	59	7,600
1,2-PB	88	6	6	8,000

[a]Determined by SEC with laser scattering detector.
[b]Determined by ^{13}C NMR.

Characterization methods

Thermal gravimetric analysis: PBs were studied using a TA Instrument Hi-Res 2,950 apparatus. Analyses were conducted on samples weighing about 10 mg, in a platinum pan, under air flowing at a flow-rate of 90 ml.min^{-1}, in an oven and 10 ml.min^{-1} of balance. The heat cycle gradient was 10°C.min^{-1} from 25 to 600°C in the air [6].

Fourier Transform Infrared Spectroscopy combined with Attenuated Total Reflection (FTIR-ATR): Infrared spectra were recorded at room temperature on a NICOLET Nexus Fourier Transform Infrared spectrometer. Recordings were obtained with a resolution of 4 cm^{-1}, and a spectral width between 400 and 4,000 cm^{-1}. ATR has a diamond crystal (128 scans) [6].

Nuclear Magnetic Resonance (NMR): The ^{1}H and ^{13}C NMR spectra were recorded using a Bruker Avance 400 MHz spectrometer in CDCl$_3$, 30°C. ^{1}H and ^{13}C NMR measurements were done at frequencies of 400.16 and 100.63 MHz, respectively. ^{1}H NMR spectra were acquired using 32 K data points, a spectral width of 4,789 Hz, an acquisition time of 3.42 s, a relaxation delay of 2 s, and a pulse width of 90° (10 μs), at 64 scans. ^{13}C NMR spectra were acquired using 131 K data points, a spectral width of 25, at 126 Hz, an acquisition time of 2.61 s, a relaxation delay of 5 s, and a pulse width 90° (8.5 μs), at 16,384 scans, and the nuclear Overhauser effect (NOE) was suppressed by gating the decoupler sequence [6].

Thermal gravimetric Analysis combined with FTIR (TGA/ FT-IR): TGA Diagrams were recorded on a TA Instrument 2,050 apparatus. Analyses were conducted on samples weighing about 10 mg, in a platinum pan, under air at a flow-rate of 90 ml.min^{-1}, in an oven, and with 10 ml.min^{-1} on the balance. The heat cycle gradient was 10°C.min^{-1} from 30 to 700°C in the air. The temperature of the transfer line was 250°C. FTIR spectra were recorded on a NICOLET Nexus Fourier Transform Infrared spectrometer. Recordings were obtained with a resolution of 4 cm^{-1} and a spectral width between 400 and 4,000 cm^{-1} (32 scans) [6].

TGA combined with thermal desorption (TD), combined with GCMS (TGA-TD/GC/MS): About 8-15 mg of samples were placed in a platinum pan of TGA. Analyses were performed under a stream of air at 45 ml.min^{-1} in an oven, and with 10 ml.min^{-1} on the balance. The heating rate of the cycles was 10°C.min^{-1} ranging from 30 to 700°C. At the oven outlet, an adsorbent tube (Tenax) was placed to trap volatile organic compounds that were within the chosen temperature range. After that, an adsorbent tube was placed on a thermal desorber.

Desorption conditions on the TD system were T (desorption): 300°C, t (desorption): 20 min, T (trap): -10°C, P (He): 99 kPa, T (trap injector): 300°C, and T (column head): 140°C. Compounds were injected and separated in a gas chromatography column with an Agilent HP of 5MS, and to the dimensions of 30 m x 0.25 mm x 0.25 μm. The oven was conducted as follows: 35°C isotherm for 15 min, 35 min at 120°C temperature rise with a gradient of 2°C min^{-1}, 120 min at 300°C temperature rise with a gradient of 3°C min^{-1}, and 3 min isotherm at 300°C. The mass spectrometer (Agilent GC-MS 6890) was adjusted for an emission current of 35 μA, and an electron multiplier voltage between 1,423 and 1,628 V. MS quad temperature was 150°C and the transfer line was set at 250°C. The ion source was 230°C. The mass range was 15-600 u [6].

Results and discussions

Thermo-oxidative degradation of 1,2 and 1,4-PB by TGA-FTIR

TGA diagrams obtained for the 1,4-PB and 1,2-PB (Fig. 1) exhibited a similar degradation profile. A mass increase began near 130°C up to 328°C for the 1,4-PB, and 375°C for 1,2-PB, which can be attributed to the oxidation of the PBs [1]. From 400°C, the PBs were rapidly decomposed with a mass loss of about 77% between 400 and 475°C. The thermo-oxidative degradation completes at 600°C. The loss of mass rapidly occurred when the temperature increased.
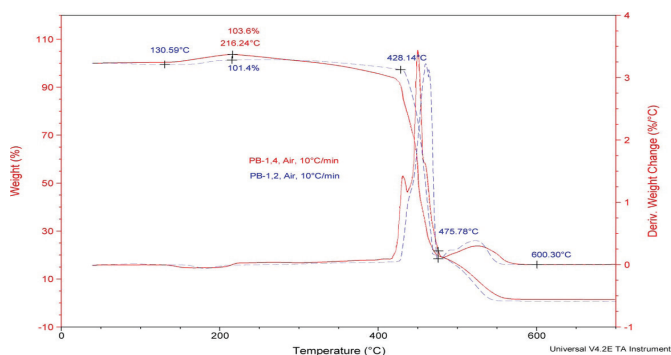

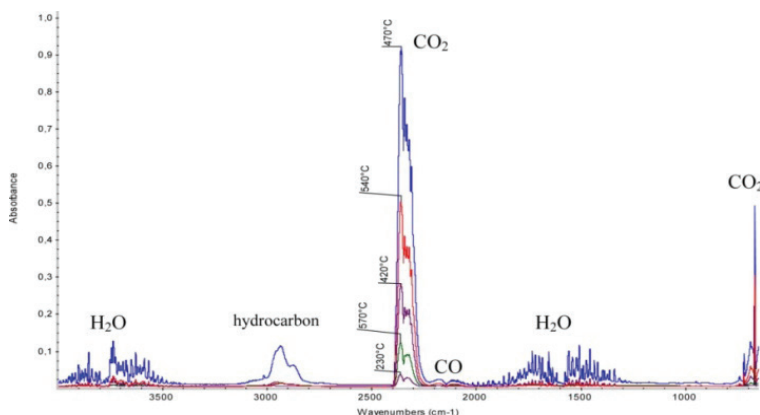**Fig. 1. TGA diagrams of 1,4-PB (red) and 1,2-PB (blue), heating 10°C.min^{-1} in the air.**

Fig. 2. FTIR spectra of volatile compounds of the 1,4-PB heated 10°C.min^{-1}, in the air.

FTIR spectra of the volatile compounds released from the TGA show that the decomposition begun at 130°C, at the same time of the oxidation. The main compounds were carbon dioxide (2,362, 2,330 cm^{-1}), carbon monoxide (2,172, 2,107 cm^{-1}), H_2O (3,739, 1,709, 680 cm^{-1}), and a low content of hydrocarbon (2,926, 2,867 cm^{-1}), as identified by FTIR.

Besides this, the FTIR spectra (Fig. 2) didn't show any volatile compounds at a temperature below 130°C. This confirmed that decomposition of PBs had not yet occurred. So, to exclusively observe the oxidation, PBs were isothermally heated at 100°C, in the air. Structural modifications during heating were monitored by FTIR, ^1H, ^{13}C NMR.

Thermo-oxidative degradation of 1,2-PB and 1,4-PB at 100°C

The previous studies showed that oxidation of polybutadiene forms a film which prevents oxygen diffusion inside materials and limits oxidation [7-8]. A thin layer of PBs was prepared on a glass surface in a solution of 5% of PBs in chloroform, and then heated at 100°C in an oven under air. Then, the samples were withdrawn at selected time intervals.

The FTIR spectra of 1,4-PB and 1,2-PB after heating at 100°C in the air (Fig. 3A, 3B) showed that the groups of 1,2-vinyl (909 cm^{-1}), 1,4-cis (729 cm^{-1}), and 1,4-trans (964 cm^{-1}) decreased. Besides this, new bands were also noted at 3,436 cm^{-1} (v_{OH}), 2,730 cm^{-1} ($v_{CH=O}$), 1,771 cm^{-1} (γ-lactone), 1,717 cm^{-1} ($v_{C=O}$), 1,177, and 1,052 cm^{-1} (v_{C-O}). These bands can be assigned to hydroperoxide, alcohol, aldehyde, carboxylic acid, ester, ketone, and ether functions.

The films after heating were soaked in a concentrated solution of ammonia for 24 hours at an ambient temperature. The FTIR spectra of the heated 1,4 and 1,2-PB showed, after
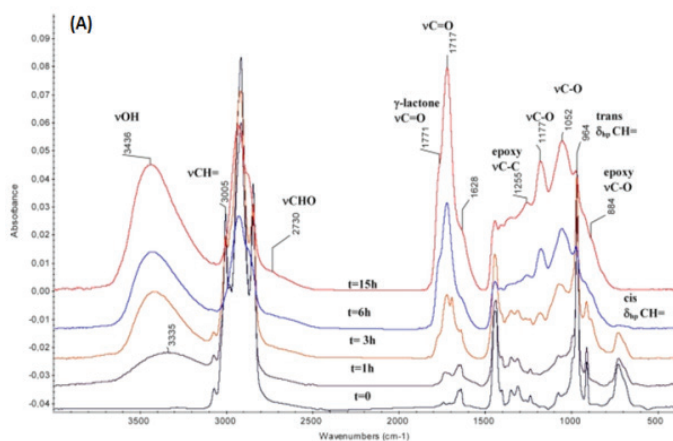

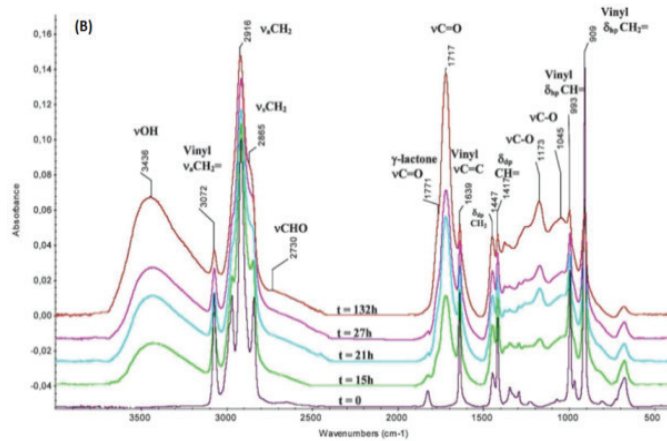**Fig. 3A. FTIR spectra (ATR-diamond) of 1,4-PB heated 100°C, in the air, t = 1, 3, 6, 15 h.**

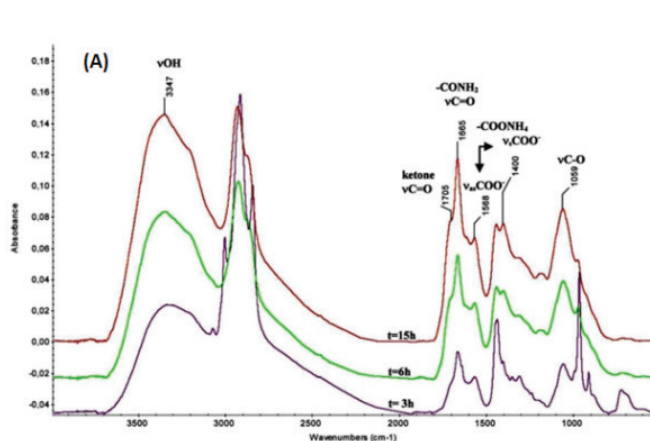**Fig. 3B. FTIR spectra (ATR-diamond) of 1,2-PB heated 100°C, in the air, t = 15, 21, 27, 132 h.**

Fig. 4A. FTIR spectra (ATR-diamond) of 1,4-PB heated 100°C, in the air, t = 3, 6, 15 h, and then derivatized with ammonia, 24 h at ambient temperature.
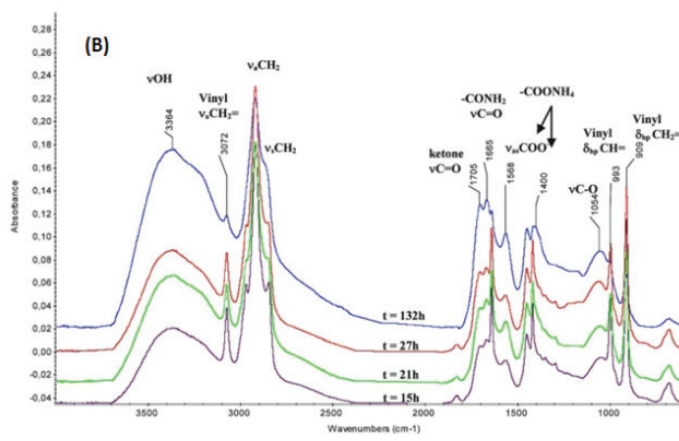

Fig. 4B. FTIR spectra (ATR-diamond) of 1,2-PB heated 100°C, in the air, t = 15, 21, 27, 132 h, and then derivatized with ammonia, 24 h at ambient temperature.

derivatization with ammonia (Fig. 4A, 4B), that the appearance of the primary amide group corresponding to bands at 1,665, 3,214, 3,347 cm^{-1} and the disappearance of the band at 1,717 cm^{-1} permit to confirm a formation of a carbonyl ester function during heating of the 1,4 and 1,2-PB in the air. Two bands at 1,568 and 1,400 cm^{-1} can be assigned to asymmetric and symmetric vibrations of ammonium carboxylate, which is due to the carboxylic acid function. The band at 1,705 cm^{-1} was not changed by the action of ammonia which confirms the presence of a saturated ketone.

The ^{1}H NMR spectrum of 1,4-PB, after 3 hours of heating (Fig. 5), showed that a doublet at 9.5 ppm with a coupling constant J = 8 Hz can be assigned to a proton of an unsaturated aldehyde function (compared to CH$_2$=CH-CHO with J = 8 Hz [9]). The peak at 9.8 ppm can be attributed to protons from the saturated aldehyde function. The group of signals at 8.1 ppm can be assigned to the protons from hydroperoxide [10]. Peaks at 6.1 and 6.8 ppm correspond to the conjugated diene structure -CH=CH-CH=CH-. Peaks at 3.5 to 4.5 ppm can be attributed to protons in the carbon atoms connected to oxygen atoms with ether, alcohol, peroxide, and hydroperoxide [10]. Peaks found at around 2.7 ppm can be assigned to protons from epoxide. The ^{13}C NMR spectrum of 1,4-PB, heated for 3 hours (Fig. 6), showed that two peaks were at 201 and 194 ppm and can be respectively assigned to carbons of ketone and aldehyde functions. The intense signals at 58 ppm (CH), 32.1 ppm (CH$_2$), 29.0 ppm (CH$_2$), 23.8 ppm (CH$_2$) permit to be assigned to an epoxide ring structure (Fig. 7), which was formed as a reaction from the peroxide radical with a double bond of 1,4-cis or 1,4-trans [11]. Besides this, the ^{1}H and ^{13}C NMR (Fig. 5, 6) also showed that the dominant oxidative product was the epoxide structure. Then, the secondary oxidation of the oxidised structures had rapidly occurred.

For 1,2-PB, after 8 hours of heating, the sample could not be soluble in the solvent, causing difficulties of observation using the liquid NMR. The ^{1}H NMR spectrum of 1,2-PB, after heating at 100°C for 7 hours in the air (Fig. 8A), also permitted identification of new functional groups, such as epoxide rings, ether, hydroperoxide, and unsaturated structures (respectively at 2.62, 4.09, 8.04, 9.48 ppm) corresponding to oxidised products. This result was similar to what was found with the former IR spectra method (Fig. 3A, 3B). Besides this, an intense signal at 1.25 ppm can be assigned to a saturated structure. The ^{13}C NMR (Fig. 8B) showed that the signals at 38.7 and 40.9 ppm correspond to carbon methine (-CH-) and methylene (-CH$_2$-) of the 1,2-vinyl isomer, and had decreased after heating. The appearance of signals of CH$_2$ at 29.7 ppm and CH at 38.5 ppm permits the assignment of carbon methylene and methine of polycyclohexane like structures. The polycyclohexane structure is more stable than the 1,2-PB one. Consequently, the 1,4-PB (containing secondary allylic carbons) was more quickly
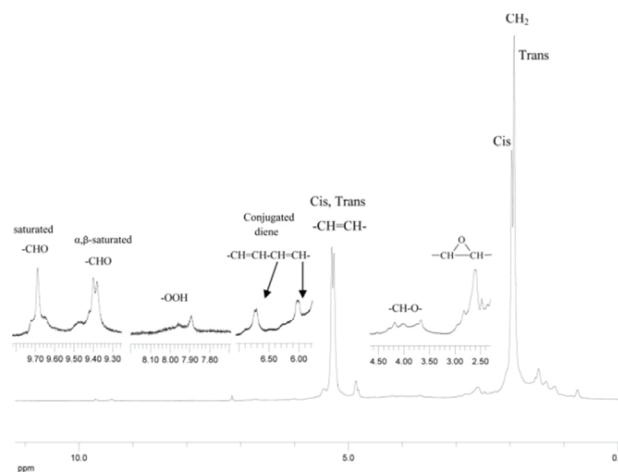

Fig. 5. ^{1}H NMR spectrum of 1,4-PB heated at 100°C, 3 h, in the air, 400.13 MHz, CDCl$_3$, TMS, 30°C.
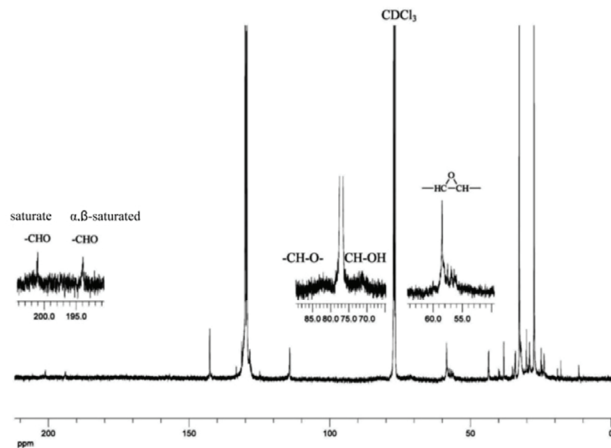

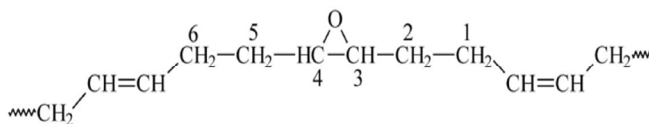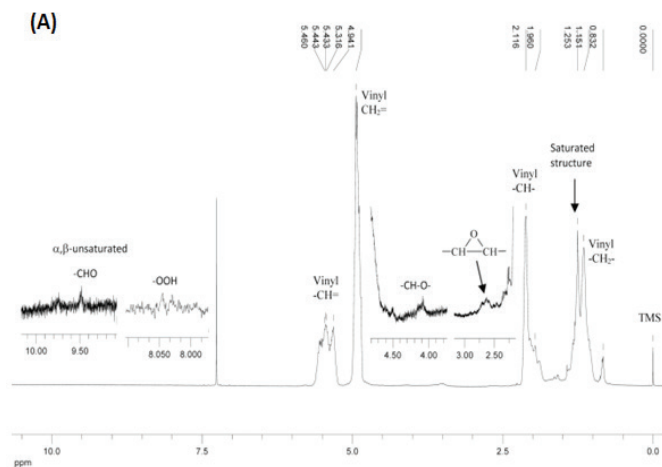**Fig. 6.** ^{13}C NMR spectrum of 1,4-PB heated at 100°C, 3 h, in the air, 100.63 MHz, CDCl$_3$, TMS, 30°C.

Fig. 7. Epoxide structure of the oxidized 1,4-PB.
C$_1$: 23.8; C$_{2,5}$: 32.1; C$_6$: 29.0; C$_{3,4}$: 58 ppm; H$_{3,4}$: 2.7 ppm.

oxidised than the 1,2-PB (containing tertiary allylic carbons) that had been also confirmed by the IR spectra (Fig. 3A, 3B).

VOCs releasing from the thermo-oxidation degradation of the PB in course of heating were trapped and identified by TGA-TD/GCMS system.

Observation of VOCs of the thermo-oxidative degradation of PB by TGA-TD/GCMS

In a temperature range from 130 to 400°C, for 1,4-PB (Fig. 9A), major products were detected, including alcohols (1-butene-2-ol, 1-pentene-3-ol, and 2-pentene-1-ol), which can

be formed from additional hydrogen on the alkoxide radicals [1, 2, 12]; aldehydes (2-butenal, 3-methyl pentanal, 4-hexene-1-al, 2-hexenal, butanedial, furfural, and benzaldehyde), which can be formed by β scission of alkoxide radicals and polycycloperoxide [1]; ketones (2-butanone, 1-pentene-3-one, 3-pentene-2-one, cyclopentanone, 2-cyclopentene-1-one,

and 2-cyclohexene-1-one), which can be formed from "cage" reactions between alkoxide radicals and hydroxide radicals; and carboxylic acid (acetic acid, etc.), which can be formed by oxidation of an aldehyde [12].

For 1,2-PB (Fig. 9B), VOCs are mainly as follows: 3-butene-

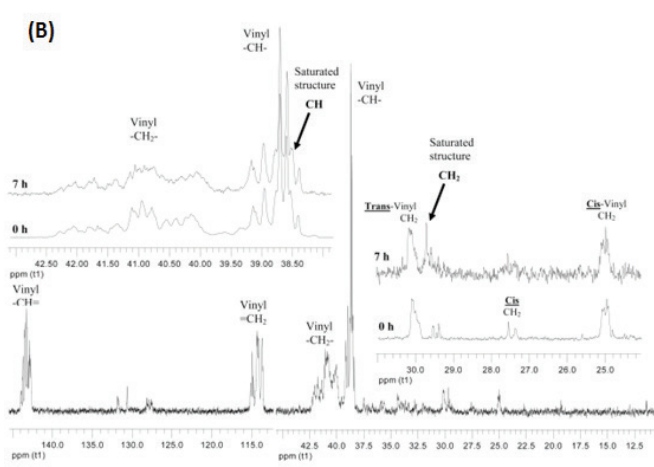**Fig. 8A.** ^{1}H NMR spectrum of 1,2-PB heated at 100^{0}C, 7 hours, in the air, 400.13 MHz, CDCl$_3$, TMS, 30^{0}C.

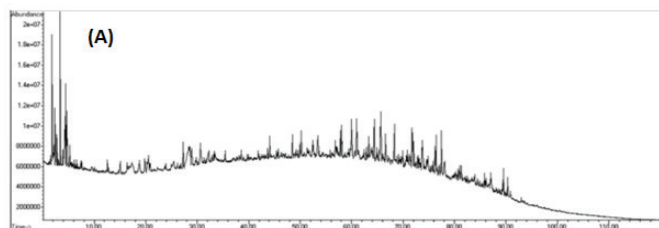**Fig. 8B.** ^{13}C NMR spectrum of 1,2-PB heated at 100^{0}C, 7 hours, in the air, 400.13 MHz, CDCl$_3$, TMS, 30^{0}C.

Fig. 9A. Chromatogram of released VOCs from 1,4-PB at 130-400^{0}C, gradient 10^{0}C.min^{-1}, in the air.
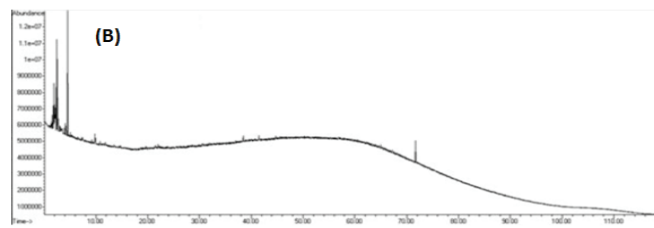
Fig. 9B. Chromatogram of released VOCs from 1,2-PB at 130-400^{0}C, gradient 10^{0}C.min^{-1}, in the air.
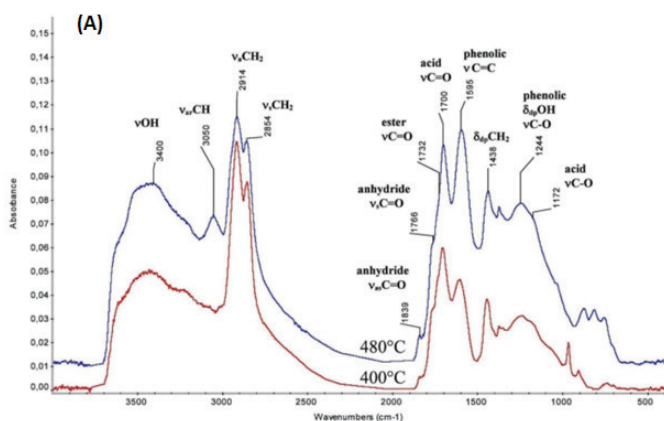
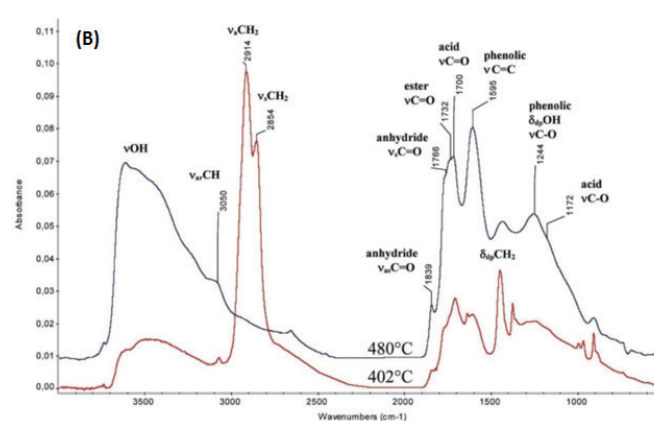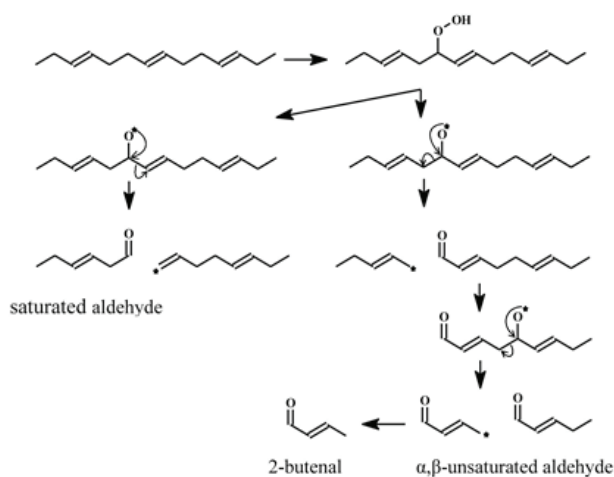**Fig. 10A.** FTIR spectra (ATR-diamond) of residues at 400^{0}C, 480^{0}C of 1,4-PB heated 10^{0}C.min^{-1}, under the air.

Fig. 10B. FTIR spectra (ATR-diamond) of residues at 402^{0}C, 480^{0}C of 1,2-PB heated 10^{0}C.min^{-1}, under the air.

Scheme 1. Formation of saturated and α,β-unsaturated aldehydes from the oxidation of 1,4-PB.

Scheme 2. Formation of saturated, α,β-unsaturated aldehydes and conjugated diene structure from the oxidation of 1,4-PB.

2-ol, 3-butene-2-one, 2-butanone, acetic acid, 2-butenal, 2-methyl 2-butenal, butanedial, 3-methyl 2,5-furandione, benzaldehyde, phenol, acetophenone, 3-methyl phenol, 4-methyl benzaldehyde, and phthalic anhydride.

The analytical results showed that the thermo-oxidative degradation of the 1-4 and 1-2 PB have differently occurred in the region below 400°C.

In a range from 400 to 600°C, volatile compounds were trapped and identified by TGA-FTIR and TGA-TD/GCMS. The main compounds were CO_2, CO, H_2O, and some hydrocarbons and the same for both 1,4 and 1,2-PB, which is comparable to the former observed in an inert atmosphere [6-13]. At high temperatures, under N_2, PBs can rapidly decompose [6-13]. In this study, the decomposition of PBs had also occurred, but there was not a participation by oxygen. The hydrocarbon residues showed that the competition between two reactions seemed to belong to the rate of oxygen diffusion on the surface of the sample and the oxygen concentration in the oven of TGA.

The residues from the thermo-oxidative degradation of PBs were obtained by performing a TGA analysis in an air flow at 10°C.min⁻¹, and stopped at 400°C and 480°C. The FTIR spectra of the 1,4 and 1,2-PB residues (Fig. 10A, 10B) showed the appearance of bands corresponding to the phenolic structures (v_{OH} between 3,000 and 3,700 cm⁻¹, $v_{C-H\ aromatic}$ at 3,050 cm⁻¹, $v_{C=C\ aromatic}$ at 1,595 cm⁻¹, and v_{C-O} at 1,244 cm⁻¹), carbonyl anhydride (1,839, 1,766 cm⁻¹), ester (1,732 cm⁻¹), and carboxylic acid (1,700 cm⁻¹). This result showed that above 400°C, thermo-oxidative degradation has rapidly occurred. The oxidative products have been already formed and continuously oxidised. Consequently, oxidised products could not be detected by GCMS.

Proposed reaction mechanisms

Based on these analytical results, some reaction mechanisms could be proposed as follows:

Oxidation on 1,4-PB: The hydroperoxide could be easily formed on allylic carbon (Scheme 1). The alkoxide radical was formed by the decomposition of this hydroperoxide. Saturated and unsaturated aldehyde products can be explained by β-Scisson of the alkoxide (Scheme 1, 2). The direct reaction of an oxygen molecule with an allylic carbon and an adjacent double bond led to form the conjugated diene structures (Scheme 2).

Oxidation on 1,2-PB: Two products 3-butene-2-ol and 3-butene-2-one formed from the thermo-oxidative degradation of 1,2-PB, allowing the consideration of two targets of oxidation on 1,2-vinyl, which are methylene (CH_2) and methine (CH) carbons. The radical attack of a hydrogen of the methylene group (CH_2) led to the formation of a radical, which was added to an oxygen molecular and a proton, forming a hydroperoxide. Then, the hydroperoxide compound is decomposed to aldehyde and alcohol by β-scission (Scheme 3A). The formation of the 3-butene-2-ol compound can be explained by rupture of the C-C bond of the alcohol I, followed by addition of a proton as shown in the Scheme 3B.

A radical will attack to the hydrogen on a tertiary CH group of 1,2-vinyl, forming a molecular radical. The addition of an oxygen molecule and a proton leads to the formation of a hydroperoxide, the decomposition of which forms alkoxide and hydroxide radicals. The decomposition of the epoxide ring formed from the alkoxide radical gives 3-butene-2-one and 2-butenal compounds (Scheme 4).
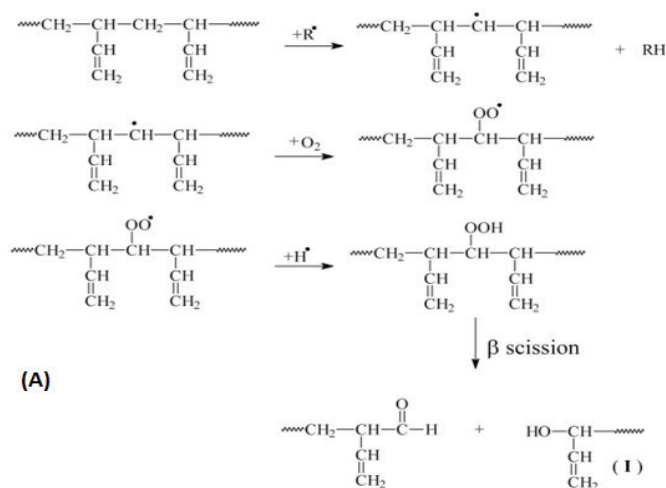
**Scheme 3A. Oxidation of the CH₂ carbon of 1,2-vinyl.**
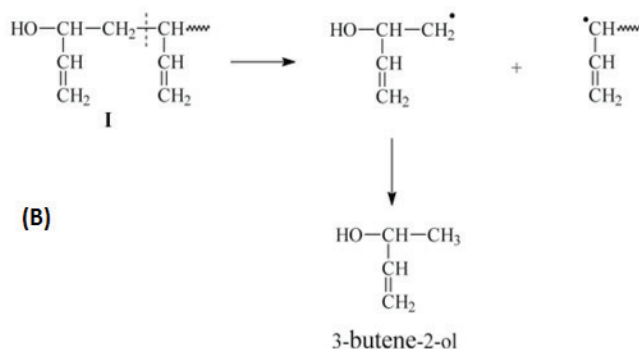
Scheme 3B. Formation of 3-butene-2-ol.
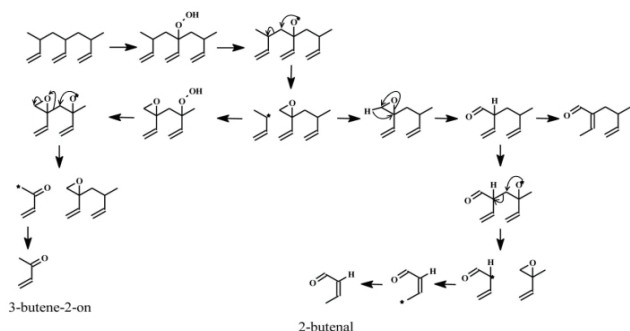
Scheme 4. Formation of 3-butene-2-one and 2-butenal.

The tertiary allylic carbon on the 1,2-PB was dominant for the formation of a tertiary stable radical. The allylic resonance between the radical and allylic double bond formed a new radical which reacted with the adjacent 1,2-vinyl groups. Consequently, the polycyclohexane-like structure had been formed (Scheme 5).
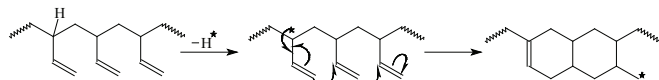
Scheme 5. Formation of polycyclohexane like structure from 1,2-PB.

Conclusions

The thermo-oxidative degradation of polybutadienes with various structures was studied and their different degradation mechanisms were discussed. Below 400°C, the oxidation of 1,4 and 1,2-PB released products with the same functions, such as ketone, alcohol, aldehyde, ester, carboxylic acid, and anhydride by different radical mechanisms. For 1,4-PB, oxidation starts on the methylene (CH₂) carbon of the 1,4 group. The dominant oxidised structure was the epoxide ring. For 1,2-PB, targets of oxidation were methylene (CH₂) and methine (CH) carbons of 1,2-vinyl. The polycyclohexane-like structure was also identified in the oxidation process of the 1,2-PB. Above 400°C, the oxidation of PB rapidly occurred. This stage corresponds to the oxidation of oxidised structures. The major products detected were carbon dioxide, carbon monoxide, water, and some hydrocarbons and aromatics for both 1,4 and 1,2-PB. Oxidation and thermal degradation took place at the same time. Their competition may belong to the rate of oxygen diffusion and oxygen concentration. This result will help to adapt the production of various synthetic rubbers and latex for suitable uses.

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