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Thermal behavior of partially hydrogenated polydienes by *p*-toluenesulfonylhydrazide

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Abstract The hydrogenation of natural rubber (NR), polybutadiene (BR), and styrene-butadiene (SBR) rubbers with different microstructures was performed by a diimide hydrogenation agent generated in situ by a non-catalytic method [1–3]. Many properties of the material depend considerably on variables such as degree of hydrogenation and proportions of vinyl or phenyl units. The mobility of the hydrogenated chain was investigated by differential scanning calorimetry (DSC) and the results confirm the relationship between the degree of hydrogenation and chain flexibility. The flexibility of a high *cis*-1,4 BR hydrogenated sample, was significantly changed and a melting point (T_m) was detected after a certain degree of hydrogenation. Thermal stability was investigated by thermogravimetric analysis (TG) and an increase was found, but, the thermal resistance was influenced by the presence of the byproduct *p*-toluenesulfinic acid. Oxidation stability was investigated by chemiluminescence analysis and it improved with hydrogenation.

Keywords Hydrogenation · Polydiene rubbers · *p*-Toluenesulfonylhydrazide · Thermal properties

Introduction

Hydrogenation has been confirmed to improve the thermal and oxidative stability of polydienes due to the reduction of the unsaturated units [1–3]. The polydiene hydrogenation methods involve catalytic and non-catalytic procedures [4–8]. Parker et al. [9] observed a large broad endothermic peak for hydrogenated SBR latex consistent with the melting of a wide variety of polyethylene segments size. They also detected higher oxidation resistance for this sample which was associated with the decreasing of allylic hydrogen present. Xie et al. [10] observed a similar behavior for catalytic hydrogenation of NBR. Phinyocheep et al. [3] studied the hydrogenation using *p*-toluenesulfonylhydrazide (TSH) for isoprene–styrene diblock copolymer and found an increase of 10–20 °C in glass transition for hydrogenated samples as well as an improved thermal stability. Samran et al. [2] applied non-catalytic hydrogenation for NR and observed a mass loss for NR hydrogenated sample starting at around 100 °C, but the total decomposition temperature is around 450 °C, which was higher than that of NR (about 350 °C). In this work the behavior of NR, high *cis*-1,4 BR, BR with high vinyl content (54 and 66% 1,2 content) and SBR with high vinyl content (32 and 62% 1,2 content) was investigated regarding the non-catalytic method in order to obtain model polymers with a different degree of hydrogenation. All the samples were commercial and had a high molecular weight. The rubbers were hydrogenated by using diimide generated in situ from the thermal decomposition of TSH [11]. The reaction is homogeneous and performed under nitrogen gas at atmospheric pressure using a relatively simple apparatus. The molar ratio TSH/C=C was 0.5, 1, and 2 and the temperature was fixed at 112 and 130 °C. The degree of hydrogenation was qualitatively monitored

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by FTIR analysis and the degree of hydrogenation was determined by the iodometry method and ^{1}H NMR analysis. Thermal behavior was monitored by differential calorimetry analysis (DSC), thermogravimetric analysis (TG), and chemiluminescence analysis (CL). The main objectives of this study were to optimize the reaction conditions to apply to commercial polydienes such as NR, BR, and SBR and to obtain wide range information about the thermal property of new materials formed.

Experimental

Materials

Commercial natural rubber, (NR Pale Crepe), high *cis*-polybutadiene (*cis*-BR), polybutadiene with different amount of 1,2 units (BR 47 and BR70) and styrene-*co*-butadiene rubber also with two different amounts of vinyl content (SBR32 and SBR62) were supplied by Bayer AG, Germany, and used without further purification. Some characteristics of the samples are shown in Table 1. The TSH was obtained from Aldrich Chemical Co. (97%, mp 108–110 °C) and the solvents were used as purchased (Aldrich, ACS reagent). In this work, the samples are designated as H_NR_X or H_BR47_X, where H indicated hydrogenated samples and X the degree of hydrogenation.

Hydrogenation procedure

Hydrogenation was carried out in *o*-xylene or xylene solution by using TSH as a precursor for diimide generation under inert atmosphere and reflux. The solution was heated at 112 or 130 °C under stirring and a molar ratio TSH/C=C of 0.5, 1.0, and 2 was added. Samples were removed at different reaction times and precipitated in methanol. The hydrogenated rubbers were purified by re-dissolution in an appropriate solvent, re-precipitated, and dried at 40 °C under vacuum.

Table 1 Rubbers used in this study

Commercial name	Name used	1,2 unit[a]/ mol%	Styrene[a]/ %	M_w[b]
NR	NR		–	2,17,9500
CB24	*cis*BR	<3	–	527,060
VI47-0	BR47	54	–	475,680
VI70-0	BR70	66	–	496,360
VSL 2525-0	SBR32	32	25	206,600
SSBR2163	SBR62	62	21	214,800

[a] Determined by ^{1}H NMR

[b] Determined by gel permeation chromatography (GPC) using polystyrene as standard

Characterization

The chemical structure of the unmodified and modified rubbers was monitored by Fourier transform infrared, FTIR, using an FTIR Instrument (Model Nicolet 60-Nexus). The FTIR spectra of the samples were obtained on films casted from toluene on NaCl plates. The resolution used was 4 cm^{-1} and 32 scans were recorded [3, 4, 8, 10, 11]. The degree of hydrogenation was determined by hydrogen nuclear magnetic resonance spectroscopy [12–15], ^{1}H NMR, and by iodometry method [10–12, 16]. The ^{1}H NMR analyses were recorded in an NMR Spectrometer (Varian 300 MHz) and the samples were dissolved in $CDCl_3$. Chemical shift was reported in ppm relative to tetramethylsilane (TMS). The iodometry method, Wijs method, was performed as reported in the literature [11, 12]. The presence of byproducts formed by the TSH decomposition was controlled by FTIR [9, 11] and by ^{1}H NMR.

Thermal stability was investigated by TG [3] using a Thermogravimetric analyzer (TA Instruments-Hi-Res TGA 2950), at 10 °C min^{-1}, under nitrogen flow, from room temperature to 600 °C. The maximum decomposition temperature (T_{max}) of each sample was obtained from the peak maxima of the derivative of the DTG curve. The variation in the chain flexibility was monitored by differential scanning calorimetry, DSC (TA Instruments—Modulated DSC 2920), at a heating rate of 10 °C min^{-1} under N_2 atmosphere in aluminum pans. The temperature range used for the analysis depends on the chemical nature of the rubber as well as on the degree of hydrogenation of the sample. The glass transition (T_g) and the melting temperature (T_m) were determined from the second scan. The error bars were put in graphics, but, due to small variation and the scale of the graphs, it appears only in some cases.

The heats of fusion (ΔH_f) were determined from the areas of the melting peaks. Oxidation resistance was investigated by CL. The measurements were performed in Atlas Chemilume CL400 equipment. Samples were put on aluminum pans in the oven-like cell, which were then closed tightly. A lens covers the sample in order to focus on the light emission. The analysis was carried out under low oxygen flow atmosphere at a defined temperature range from 120 to 165 ± 2 °C. The light emission was detected by the high-sensitive photomultiplier tube (PMT), calibrated with a constant radioactive standard intensity (approx. 10 μC) [17].

Results and discussion

Through hydrogenation saturated segments are originated in the polymer chain. Depending on the degree of hydrogenation, materials resemble PP (polypropylene) or alternating poly(ethylene-*co*-propylene) rubber can be formed if natural rubber (NR) is used as matrix material [18]. Polybutadiene polymers with *cis* and *trans* 1,4 units and 1,2 vinyl units can form materials similar to polyethylene (PE) or poly(ethylene-*co*-butylene) [19], depending on the degree of hydrogenation and the structure of the primary polymer chain.

FTIR analysis

FTIR analysis of the NR and H_NR, Fig. 1a shows a decrease and subsequent disappearance of the band at 836 cm^{-1}, attributed to C–H out of plane deformation of the trisubstituted olefinic of polyisoprene, as well as the band at 1600 cm^{-1} attributed to double bonds. Besides, a band appears at 735 cm^{-1}, related to vibration of the $–CH_2$ groups, typical for polyolefin structures like polypropylene and polyethylene. H_*cis*BR sample, Fig. 1b, show the disappearance of the band at 735 cm^{-1} (characteristic vibration for *cis*-1,4), and the appearance of the band at 720 cm^{-1}, associated with the amorphous phase and another at 730 cm^{-1}, associated with the crystalline phase, both characteristic $–CH_2–$ rocking vibrations of polyethylene segments [12, 16]. As the hydrogenation proceeds it is possible to detect first the amorphous phase and subsequently the crystalline phase. Hence, the material properties, such as degree of crystallinity, can be controlled by degree of hydrogenation. BR47, BR70, SBR32, and SBR62 samples show similar behavior in the FTIR analysis. After the hydrogenation, Fig. 1c, these samples show a gradual decrease in the intensity of the bands at 966 cm^{-1} (characteristic vibration of the *trans*-1,4 units presents in the BR microstructure), at 994 and 910 cm^{-1} (characteristic vibration of the 1,2 vinyl units presents in the BR microstructure) and at 758 cm^{-1}, characteristic of *cis*-1,4 units. Simultaneously, there is the appearance of a band at 720 cm^{-1} attributed at $–CH_2–$ rock vibration [5].

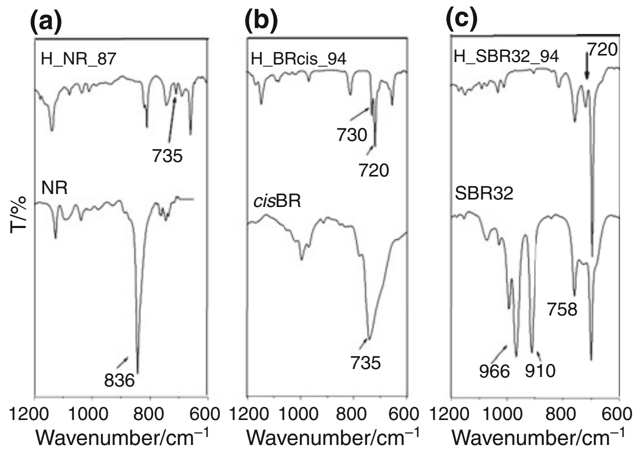

Fig. 1 FTIR spectra of (**a**) NR, (**b**) *cis*BR and (**c**) SBR32 samples, non-hydrogenated and hydrogenated samples

Flexibility of the hydrogenated samples

As previously reported, in the FTIR analysis, the hydrogenated samples show variations with respect to the microstructure when compared to the primary polymer. Figure 2 shows the new saturated segments formed, depending on the amount and how they are arranged in the molecule, which affect differently the thermal properties of the material. In H_NR a small increase in the T_g was observed indicating that the chain flexibility has not varied significantly. H_NR_87 in condition TSH/C=C of 2/1 at 112 °C shows only a 6.3 °C increase in T_g related to NR. In the case of H_SBR32, the influence of the modification is more pronounced depending on the reaction conditions applied. In our studies a 12 °C variation was observed for H_SBR32_94 (TSH/C=C 2/1 at 112 °C). Similar results were reported by Sarkar et al. [14] in the catalytic hydrogenation of SBR latex. In H_SBR32, (TSH/C=C 0.5/1 at 112 °C) a gradual increase of T_g can be seen with the degree of hydrogenation, Fig. 2. The variations observed in the behavior of the materials as a function of reaction conditions, especially with a higher amount of TSH and at a higher temperature can be associated with the presence of byproducts and/or intermolecular rearrangement like hydrogen bonds.

H_*cis*BR presented a sharp increase in T_g, no longer showing a glass transition, but a first order transition attributed to melting temperature (T_m), which should be associated with the presence of crystalline structures,

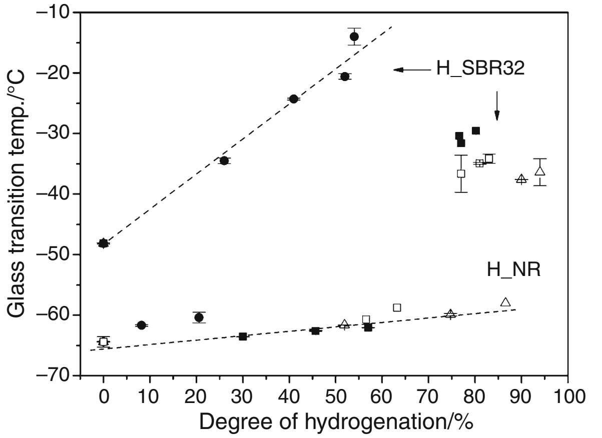

Fig. 2 Glass transition temperatures as a function of degree of hydrogenation for NR (*filled circle* 0.5/1, *filled square* 1/1, *open triangle* 2/1 at 112 °C, and *open square* 1/1 at 130 °C) and SBR32 (*filled circle* 0.5/1, *filled square* 1/1, *open triangle* 2/1 at 112 °C, and *open square* 1/1 at 130 °C). PS: The error bars were put in graphic, but, due to the scale of the graph, it appears in some cases

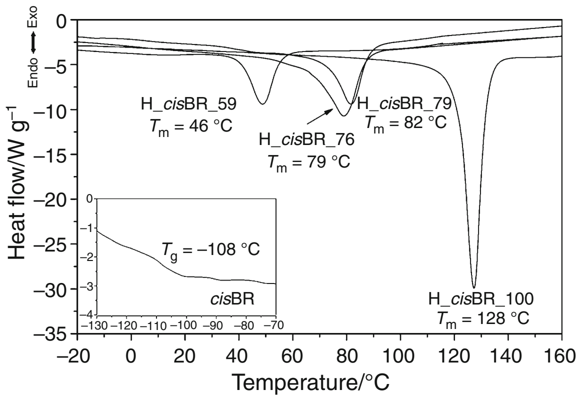

Fig. 3 DSC thermograms of *cis*BR and H_*cis*BR with 59, 76, 79, and 100 mol% degree of hydrogenation

Fig. 3. This behavior is in agreement with the FTIR analyses where these samples show a band at 730 cm^{-1} related to –CH$_2$ groups typical of crystalline phases. It was observed that the initial transition, characterized by T_g at −108 °C, changed abruptly and a melting point appeared at degrees of hydrogenation above 50%. A gradual rise in the T_m value could be observed with the increase of the degree of hydrogenation. This was observed in molar ratio TSH/C=C 1 and 2/1 and a temperature of 112 and 130 °C. Another important observation is the similarity between the T_m value determined for H_*cis*BR_100 and the T_m value of high density polyethylene (HDPE, 128 °C approximately). These facts confirm that it is possible to form new materials through the controlled hydrogenation of polydienes, whose thermal properties will be similar to a polyethylene.

As is known, endothermic peaks are associated with the presence of crystallites in DSC analysis. The area of these peaks provides us information about the degree of crystallinity of the material. The degree of crystallinity (X_c) was calculated according to the following equation [20]:

$$X_c\ (\%) = \left(\frac{\Delta H_{\text{sample}}}{\Delta H_{\text{standard } 100\%}}\right) \times 100,$$

where ΔH is the heat of fusion (J g^{-1}) of sample investigated and ΔH standard 100%, the heat of fusion of a 100% crystalline PE ($\Delta H_{PE} = 293$ J g^{-1}) [18, 21]. An increase in crystallinity is observed with the increase in the degree of hydrogenation. Probably, the obtained of longer ethylene segments favored the formation of a crystallite structure as a consequence of ordering parts of the polymer chain. In H_*cis*BR_95, a similar degree of crystallinity compared with high density polyethylene (HDPE) could be found as can be observed in Table 2 that shows the degree of crystallinity (X_c) calculated for H_*cis*BR samples with variable degrees of hydrogenation.

Table 2 Degree of crystallinity (X_c) calculated by DSC analysis

Samples	Degree of hydrogenation/%	ΔH_{sample}/J g^{-1}	X_c/%
H_BR	38	10	3
	59	28	9.6
	73	49	17
	75	54	18
	78	62	21
	95	157	54
HDPE	–	158	54

$\Delta H_{\text{standard}}$ of PE = 293 J/g [18, 21]. Rate 10 °C/min; value obtained in the second run

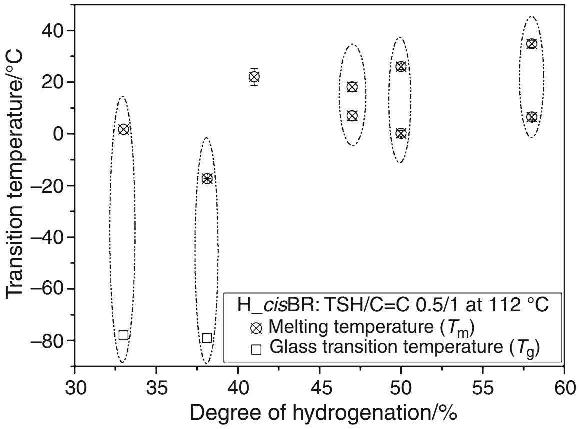

Fig. 4 Thermal behavior of high *cis*BR samples as a function of degree of hydrogenation. PS: The error bars were put in graphic, but, due to the scale of the graph, it appears in some cases

In order to follow the behavior of the T_g and the T_m of the high *cis*BR as a function of degree of hydrogenation, an experiment was carried out under mild conditions, TSH/C=C 0.5/1 at 112 °C. The results are shown in Fig. 4. It easy to see that between 30 and 40% of the degree of hydrogenation, two distinct transitions were detected: one related to the glass transition and the other attributed to melting transition. Between 40 and 48% of hydrogenation only one peak associated with T_m peak of the material was detected. As the hydrogenation proceeds, two T_m peaks can be visualized, which are better defined in a higher degree of hydrogenation. We attributed this fact to the formation of variable-sized crystallites from different segments of polyethylene. Hence, the region at 40–48% of hydrogenation is the threshold region between the amorphous phase and the crystalline phase.

In our study, we observed that the hydrogenation reaction of polybutadiene using TSH as promoter of diimide under given conditions was extremely rapid, resulting in a sharp modification of the molecular structure of rubber. We also observed that under controlling reaction conditions such as low molar ratio TSH/C=C (0.5/1), low temperature and short reaction times the evolution of the change in microstructure as a function of hydrogenation could be monitored.

In H_BR47, H_BR70, H_SBR32, and H_SBR62, no evidence of any crystallization phenomenon was observed, only a glass transition temperature, which increase significantly and gradually. In the case of H_BR47_53 and H_BR70_60 an increase of 49 and 54 °C were observed, respectively, under condition TSH/C=C 0.5/1 at 112 °C. H_SBR32_54 and H_SBR62_49 under the same condition, showed a rise of 34 and 30 °C, respectively, for their T_g. Hence, the samples with the highest level of 1,2 units exhibit a higher glass transitions temperature without crystallization. This is related to the amount of 1,2 units present in the microstructure of the primary polymer, which, according to the literature [22], is introduced in order to prevent the crystallization of the material, even for a high percentage of modification. It can be associated with side groups that have only two carbons and a planar displacement which required a greater free volume to move. Parker et al. [23] report that the presence of styrene in the SBR samples also difficult the crystallite formation, which is too large to be incorporated into a polyethylene crystallite. The presence of styrene in the SBR62 samples, about 21%, also influenced the mobility of the polymeric chain. Comparing H_SBR62_43 with H_BR70_49 we can observe that the H_SBR62 sample required more energy to move its polymer chain than the H_BR70 sample. It was shown through the increase of 30 and 21 °C in T_g, related to the parent polymer for H_SBR32_43 and for H_BR70_49, respectively.

Stability of the hydrogenated rubbers

The literature [10, 14] reported that hydrogenation of the polymer improved the thermal and oxidative stability as compared to the primary polymers. To assess this property, hydrogenated and non-hydrogenated samples were analyzed by TG, evaluating the variation in the maximum temperature through the DTG curve. Thermograms of NR and H_NR_87 are shown in Fig. 5, together with the respective DTG curve. For H_NR_87 the maximum decomposition temperature (T_{max}) of the DTG curve was shifted from 376 (T_{max} of NR) to 452 °C, indicating an improvement of thermal stability in the hydrogenated sample.

Figure 6 shows the T_{max} values as a function of the degree of hydrogenation for the different rubbers studied. It should be recalled that through the hydrogenation, materials with similar characteristics of EPDM, PP, and PE can be formed. Commercial samples of EPDM1070, PP, and HDPE were also analyzed by TG and the results were plotted in Fig. 6.

In the case of NR, a high increase of T_{max} was observed for the first 20 mol% of hydrogenation (H_NR_20) followed by a continuous increase with the degree of hydrogenation. This confirms the effect of hydrogenation in improving the resistance in the thermal stability of materials. On the other hand, the DSC analysis of these samples showed that there was no loss of flexibility, so, thermal stability was improved through the hydrogenation, without loss of elasticity of the material. Another important observation is the T_{max} observed for H_NR_87, 452 °C, that is equal to the value obtain for the EPDM1070 (452 °C) and close to the polypropylene (PP), 446 °C. These results corroborate the similarity achieved in the thermal stability of H_NR_87 to polyolefin's. In the case of H_*cis*BR and H_SBR32 samples, a continuous increase in T_{max} with hydrogenation is also observed. The T_{max} determined for H_*cis*BR_95 was 475 °C, very close to the value determined for HDPE (472 °C). This approach confirms the presence of segments of polyethylene in the hydrogenated polymer chain, as was also discussed in the FTIR and DSC analysis. Unexpectedly, H_SBR32 samples, as well as H_BR47 and H_BR70 samples, showed a decrease in thermal stability. This must be associated with the presence of the byproduct (*p*-toluenesulfinic acid)

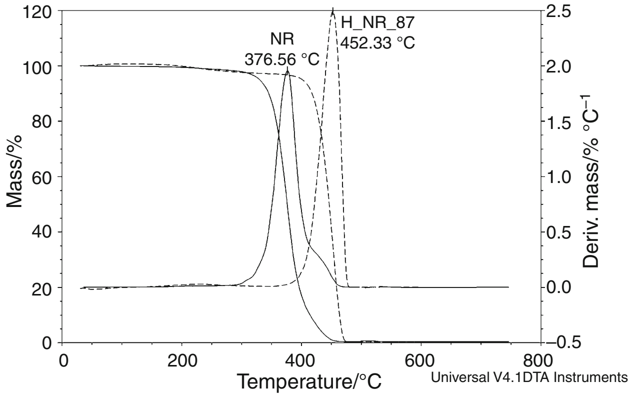

Fig. 5 TG and DTG curves of the NR and H_NR_87 samples

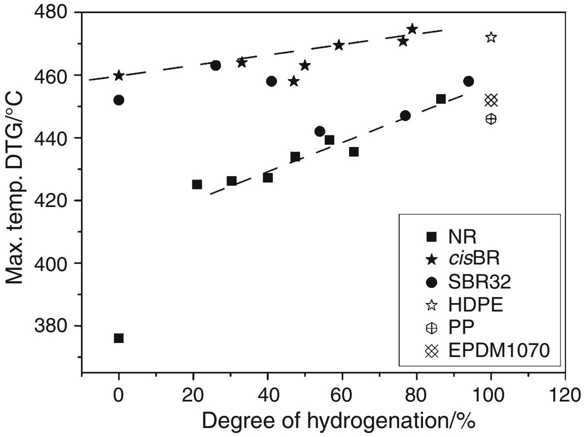

Fig. 6 Maximum decomposition temperature value obtained through the DTG curve of NR, *cis*BR, SBR32 and its hydrogenated samples, such as HDPE, PP and EPDM1070 samples

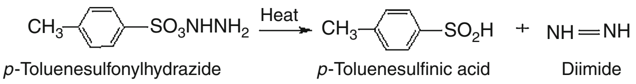

Fig. 7 Schematic representation of thermal decomposition of TSH reagent

attachment to the polymer chain [4, 6, 15], which may provoke acceleration in the pyrolysis process of the samples, making them less stable to temperature.

It is already known in the TG analysis that the products with low molecular mass are primarily decomposed, following the polymeric substrate. In hydrogenation by TSH two main products are formed, the hydrogenated polymer, and the *p*-toluenesulfinic acid. In order to better understand the reason for the lack of stability for some samples, the TSH reagent was also analyzed by TG. A total mass loss was observed until 320 °C. The thermogram showed two defined peaks, one at 170 °C and another at 265 °C. If a relationship is established between the thermal degradation reaction of TSH, Fig. 7 and the peaks observed in the DTG curve in the TG analysis, the first peak at 170 °C can be associated with a diimide fragment and the peak around 265 °C with *p*-toluenesulfinic acid.

Monitoring the total mass loss percent until 320 °C, in some cases, as in H_BR47 and H_BR70, Table 3, an increase was found in this value and a decrease in the maximum decomposition temperature (T_{max}). The phenomenon was more pronounced for the samples in which a high amount of 1,2 units, even under condition TSH/C=C 0.5/1 at 112 °C. The behavior can be associated with byproduct attached to the polymer chain which affects the stability of polymeric materials.

Oxidation resistance

Information about the oxidation resistance of hydrogenated materials was obtained by evaluating induced oxidation temperature (OIT) in the Chemiluminescence's (CL) analysis. Figure 8 shows chromatograms of *cis*BR and H_*cis*BR_97 obtained by CL-OIT analysis and the results show that the hydrogenated sample has a higher OIT value than the pure BR sample. Table 4 records the OIT results for *cis*BR, SBR32 and their hydrogenated samples. The results confirm that the hydrogenated sample has better oxidation resistance than the analogous rubber. Some samples, such as H_*cis*BR_59, showed two events. One explanation for this could be the presence of heterogeneity in a microstructure of these samples, including amorphous regions, most prone to oxidation, and crystalline regions, associated with a non-uniform partial hydrogenation. It must be remembered that this sample also showed two transitions in the DSC thermograms and the typical bands for amorphous and crystalline phases in the FTIR analysis.

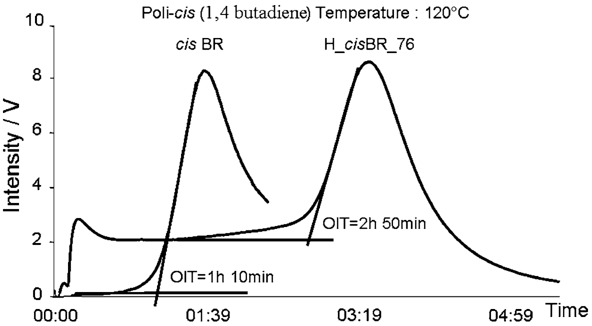

Fig. 8 Chemiluminescence analysis of *cis*BR and H_*cis*BR_76

Table 4 Induced oxidative temperature (OIT) obtained by chemiluminescence analysis (CL)

	Hydrogenation/%	OIT by CL/min
*cis*BR	–	68
H_*cis*BR	59	–[a]
H_*cis*BR	76	169
H_*cis*BR	97	284
SBR32	–	185
H_SBR32	50	–[a]
H_SBR32	79	292

[a] Presence of two events in the chemiluminescence analysis

Conclusions

Non-catalytic hydrogenation using TSH is an efficient method to hydrogenate polydienes rubbers such as NR, BR,

Table 3 Relation between degree of hydrogenation, maximum decomposition temperature (T_{max}) in the DTG curve, and total mass loss (%) at 320 °C in H_BR47 and H_BR70 samples under condition TSH/C=C 0.5/1 at 112 °C

H_BR47			H_BR70		
% Hid	T_{max}/°C	Mass loss % at 320 °C	% Hid	T_{max}/°C	Mass loss % at 320 °C
0	451	0.05	0	454	0.1
43	462	0.8	12	458	0.6
52	445	1.9	43	443	1.9
53	442	2.4	60	452	2.7

and SBR. The hydrogenation yield depends on the temperature, molar ratio TSH/C=C, time and, especially, on the microstructure of polydienes. The high molecular mass of the primary polymer also must be considered. The hydrogenated samples showed a modification in their microstructure resembling PE, PP, or, still, EPDM segments. These new saturated segments, depending on how they are arranged in the molecule, including their percentage, affected the thermal properties. A linear increase in T_g was detected for H_NR and H_SBR. H_*cis*BR first showed a sharp increase in T_g and, depending on the reaction conditions, the appearance of T_m peak was observed, which was associated with the development of crystalline segments. The FTIR analysis also detected absorbance related to the crystalline phase. Samples with a high amount of 1,2 units recorded only T_g due to fact that the 1,2 units prevent the crystallization of the material, even for a high degree of modification. The styrene units present in the SBR also difficult the crystallization. They are too large to be incorporated into a polyethylene crystalline. Thermal stability gradually increased with the degree of hydrogenation, but some samples showed a decrease that must be due to the presence of residual byproduct fragments linked to the vinyl groups in the polymer chain. The effect is more pronounced in the samples with a high amount of 1,2 units and high degree of hydrogenation. A relation could be established between the degree of hydrogenation and the percentage of mass loss at 320 °C in the TG analysis, and this would be helpful to monitor this phenomenon. Hydrogenated samples showed a good increase in the oxidation resistance detected by the CL-OIT analyses. In some cases, two events were observed associated with the presence of heterogeneity in microstructure including amorphous and crystalline regions, not uniformly distributed in the polymer structure.

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