

Evaluation of Thermal and Mechanical Properties of Rubber Compositions Based on SBR Extended with Safe Oils

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ABSTRACT: The extender oil usually employed in compositions of rubbers based on styrene and butadiene (SBR) 1712 is the distilled aromatic extract (DAE). In this work, this oil was substituted by oils with low levels of polycyclic aromatic hydrocarbons (PAHs): treated residual aromatic extract (TRAE) and two naphthenic oils from different suppliers (HN1 and HN2). This substitution was performed in response to REACH Regulation (EC No. 1907/2006 European Parliament and the Council of December 18, 2006, Annex XVII), which state that the sum of individual PAHs should be below 10 mg/kg and the levels of benzo (a) pyrene (BaP) should not exceed 1 mg/kg. Infrared spectroscopy was employed to characterize the

structure of crude oils and respective SBR compositions. Thermal properties of the materials were evaluated by thermogravimetry and differential scanning calorimetry. Mechanical properties as tension tests, hardness, abrasion resistance, and resilience were also determined. The final results showed that it is possible to replace the extender oil DAE for any of the oils tested, specially the naphthenic HN1, without any loss of the properties evaluated in this study for the SBR compositions. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: styrene–butadiene rubber (SBR); extender oil; polycyclic aromatic hydrocarbons (PAH)

INTRODUCTION

The world market for elastomers is dominated by two types of rubber, natural rubber and butadiene–styrene rubber (SBR). Both share 70–75% of this segment, especially in applications such as tires and treads.¹

Some types of oils are added in rubber compositions to reduce their viscosity, which facilitate the processing, while also controlling physical properties as tension, modulus, elongation, hardness, etc. Usually the process oils are cheaper than the polymer and the addition of them, together with filler or reinforcement agents, reduce the cost of the compound. Nevertheless, the addition of high oil contents may compromise the final product performance.²

In general, the plasticizer employed in SBR compositions is called extender oil, which is composed by hydrocarbons molecules containing between 25 and 35 carbon atoms. Depending on the molecular

structure, these oils are basically classified into three types: paraffin, naphthenic, and aromatic.³

For a long time, the use of distilled aromatic extract (DAE) has been privileged. This oil, obtained as a byproduct in the manufacture of lubricants, is the extender oil mostly employed by tire manufacturers, due to its technical advantages as low cost and availability, factors which are very difficult to overcome. Additionally, the chemical characteristic of this oil promotes a high compatibility with SBR leading to high performance artifacts.^{4–8}

DAE contains, among its constituents, polycyclic aromatic hydrocarbons (PAH), which constitute a class of organic compounds characterized by substances that have two or more conjugated aromatic rings.⁹ The PAHs are composed of more than a hundred substances with aromatic structure, found in the environment and formed by both natural and industrial processes. PAH are produced by incomplete combustion of organic materials such as oil, gas oil, coal, and wood and can be found in various places such as air, soil, and water.^{4,10}

Some studies with these compounds showed that most of them affects drastically the environment and has great mutagenic and carcinogenic potential.⁹ The translocation of PAH in the environment occurs mainly in airborne transmission associated with fine

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The authors dedicate this work to Prof. Fernanda M.B. Coutinho, *in memoriam*.

particulate matter, allowing widespread distribution of these compounds. Once emitted into the atmosphere, these pollutants can be deposited in the dry form (vapor or particulate) or wet (precipitation in the form dissolved or particulate) in aquatic and terrestrial systems. The PAH are not degraded by most microorganisms, due to the complexity of their chemical structure and low solubility in water.⁹ Ecotoxicity studies have shown unequivocally that these particles affect, for example, aquatic organisms.^{11,12}

In 1994, attention began to focus on the fact that all the compounds present in tire rubber composition end up on the roads, soil and groundwater, in the form of free particles. In 1997, the Agency for Toxic Substances and Disease Registry (ATSDR) with the Environmental Protection Agency (EPA) released a list, known as CERCLA Priority List of substances potentially toxic to humans. From that list, EPA gave priority to 16 PAH. In the 2005 list, the substance that occupies the first place was arsenic, followed by lead and mercury. PAH, as a group of compounds, remained in seventh place, and benzo [a] pyrene and benzo [b] fluoranthene alone occupied the ninth and tenth positions, respectively.⁹

Therefore, since January 1, 2010, all European tire industries under the command of European Union (EU) had to modify their usual compositions substituting the extender oil commonly employed, DAE, to oils with low content of PAHs. According to the REACH Regulation (EC No. 1907/2006 European Parliament and the Council of December 18, 2006, Annex XVII); henceforth, the extender oils used as processing agents must combine the following parameters^{12,13}:

- (1). PAH content must be below 3.0 % by mass, according to IP346 (method that measures the amount of compounds that can be extracted by dimethyl sulfoxide (DMSO) and have a mutagenic index (MI) value obtained by the Ames test less than 1;
- (2). sum of individual PAH below 10 mg/kg;

TABLE I
Eight Carcinogenic PAH Allowed in Rubber Compositions⁶

Individual PAH	CAS number
1. Benzo (a) pyrene	50-32-8
2. Benzo (a) anthracene	56-55-3
3. Benzo (b) fluoranthene	205-99-2
4. Benzo (j) fluoranthene	205-82-3
5. Benzo (k) fluoranthene	207-08-9
6. Dibenzo (a,h) anthracene	53-70-3
7. Chrysene	218-01-9
8. Benzo (e) pyrene	192-97-2
Maximum total value	10 mg/kg

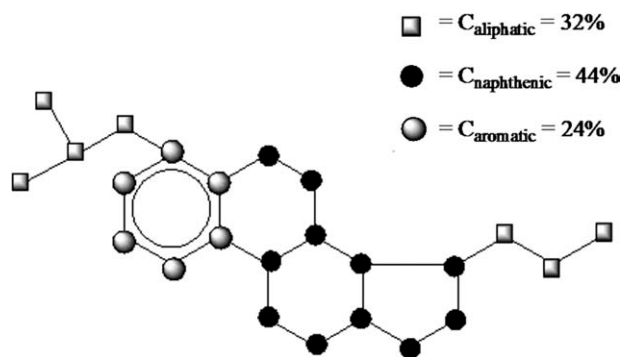


Figure 1 Hypothetical structure of mineral oil containing aliphatic, naphthenic and aromatic groups.

- (3). level of benzo (a) pyrene (BaP) should not exceed 1 mg/kg.

Eight PAHs (Table I) were identified as carcinogens and are regulated by EU legislation mentioned above.⁶ Figure 1 presents a hypothetical structure for a molecule of mineral oil.¹⁴

After the new legislation, the main issue has been focused on identifying which oil is the most suitable for substitute DAE as a plasticizer in rubber compounds, to meet the recommended specifications. Currently, the products potentially able to substitute the aromatic oil (DAE), which has been evaluated by SBR tire industries worldwide are⁷:

- heavy naphthenic oils;
- mild extraction solvate (MES): moderately refined paraffinic-based oil (the product can be manufactured by any refinery);
- treated distillate aromatic extract (TDAE): this extract comes from DAE after being refined to meet the necessary criteria;
- treated residual aromatic extract (TRAЕ): residual aromatic extracts obtained from aromatic plants with additional treatment process to reduce the levels of aromatic extracts.

The use of alternative oils extenders for SBR in tire industries is under investigation in many countries. According to the European oil companies, there are mainly two alternatives: MES and TDAE. However, problems with the availability of these oils have been verified, depending on the geographic area in question. Furthermore, a substantial investment must be done to compensate loss of performance of the materials. Thus, some tests must be carried out before a possible wide use.^{7,8,15} Therefore, the objective of this work is to evaluate the influence of three alternatives in substitution of DAE extended oil for SBR (series 1712) rubber compositions: residual aromatic extract

treated (TRAE) and two heavy naphthenic oils (HN1 and HN2).

EXPERIMENTAL

Materials

The following materials were used as received: styrene-butadiene rubber (SBR1712), random copolymer with 23.5% styrene content. SBR lattices were mixed with 27.5 part of extender oil and the systems coagulated before composition (Lanxess Elastômeros do Brasil SA); aromatic extender oils: DAE and residual aromatic extract treated (TRAE) (Lanxess Elastômeros do Brasil SA); naphthenic extender oils: heavy naphthenic oils manufactured by supplier 1 and 2 (HN1 and HN2, respectively); carbon black (Sid Richardson Carbon Co), *N-t*-butyl benzothiazole sulfenamide (TBBS) (Uniroyal Chemical Company), stearic acid (SF Sulfur Corporation), sulfur (SF Sulfur Corporation), zinc oxide (Zinc Corporation of America). Table II presents the composition employed for all formulations.^{16,17}

Methods

The following methods were employed to characterize the crude oils and SBR compositions.

Infrared spectroscopy (FTIR)

Fourier transform-infrared spectra were recorded on a Perkin-Elmer Spectrum One spectrophotometer, at a resolution of 2 cm⁻¹, in the range from 4000 to 450 cm⁻¹. Oil samples were analyzed directly without prior treatment. SBR with extension oil lattices were coagulated in methanol, dried at 60°C, and then dissolved in a 2% chloroform solution. The samples were cast in zinc selenide (ZnSe) plates. Sample solutions were exposed to mild heating for elimination of the solvent.

Thermal analysis (TG and DSC)

Thermogravimetric experiments (TG) were performed in a TA Instruments 2950 Hi-Res Analyser. Samples weighing between 5.0 and 6.0 mg were placed in a platinum-pan and heated from 50 to 650°C, at a heating rate of 10°C/min, under N₂ atmosphere. Aluminum, nickel, and perkalloy were used as standards. During the heating period, the weight loss temperature dependence (TG curves) and the respectively derivative curves (DTG) were recorded.

In this study, the onset degradation temperatures (T_{onset}) of the crude oils and rubber compositions after vulcanization were defined as the initial tempera-

TABLE II
Rubber Compound Formulation

Compounds	Formulation (g)
SBR 1712	46.750
TBBS	0.469
Carbon black	23.374
Stearic acid	0.340
Sulfur	0.595
Zinc oxide	1.020
Total	72.548

ture of degradation, corresponding to the intercept of the tangent drawn at the inflection point of the decomposition step with the horizontal zero-line of the TG curve. Peaks observed in DTG curves correspond to the temperatures at maximum rate of weight loss in the corresponding step.

Differential scanning calorimetry (DSC) was conducted in a DSC Modulated DSC 2910, under N₂ atmosphere. Prior to determining the glass transition temperature (T_g), a first scan was held, to erase the thermal and mechanical history of the samples, as follows: heating from room temperature to 100°C, at a heating rate of 30°C/min. One minute isotherm was held at 100°C, with subsequent quenching to -100°C. Ten minute isotherm was held and a new warming run from -100 to 60°C, at a heating rate of 10°C/min were performed.

Mechanical tests

Some mechanical properties of the compositions based on SBR extended in different oils were evaluated. The standard tensile tests (to determined modulus, tensile strength, and elongation at break) were performed in a Instron model 5581 dynamometer, equipped with a 1 kN load cell and pneumatic grips, according to ASTM D 412-98a.¹⁸ Tear strength was also determined in the same equipment, following ASTM D 624.¹⁹ Abrasion resistance was evaluated in a Maqtest rotating drum abrasimeter, according to DIN 53516.²⁰ The Shore A hardness was determined in a Bresser tester (durometer), according to ASTM D 2240-04.²¹ Resilience of the rubber compositions were verified in a Zwick resiliometer, according to ASTM D1054-91.²²

RESULTS AND DISCUSSION

Table III shows some characteristics, informed by the suppliers, of the four oils tested and also TDAE,²³ initially proposed as a substitute for DAE, by Bureau de Liaison des Industries du Caoutchouc Brussels (BLIC).

In this study, regardless of the oil employed, it was not observed differences in the processing of

TABLE III
Main Characteristics of Safe Oils from Different Suppliers²³

Properties	Especification BLIC for TDAE ^a	DAE	TRAE	HN1	HN2
Aromatic carbon (%)	25–30	45.0	25.0	14.9	25
Naphthenic carbon (%)	25–30	1.8	12.8	30.2	21
Paraffinic carbon (%)	42–50	53.2	62.2	54.9	54
PAH (%) ^b	2.9	19.0	1.97	1.6	Nd
PAH (ppm)	<10	99.66	2.03	<8	<10
Benzo(a)pyrene	<1	15.73	0.32	<1	<1
T_g (°C)	(–44 to –50)	–39.7	1° –39.2 2° –4.9	–54.1	–52.9

^aTreated distillate aromatic extract.

^bPolycyclic aromatic hydrocarbons.

SBR formulations, being all compositions within the specification range required for those containing DAE.

Infrared spectroscopy (FTIR)

Figure 2 shows FTIR spectra of the crude oils. The main characteristic groups absorptions presented in all spectra were: 3000–2840 cm^{-1} (asymmetrical and symmetrical axial deformations of aliphatic C–H); 1375 and 1450 cm^{-1} (angular deformations of C–H (CH_2 and CH_3); 720 cm^{-1} (asymmetrical angular deformation of CH_2). Furthermore, DAE, TRAE, and HN2 oils spectra show the presence of aromatic compounds bands: 900–675 cm^{-1} (angular deformation out of plane of C–H at ring); 1300–1000 cm^{-1} (angular deformation of C–H at ring); 1600–1585 cm^{-1} (axial deformation of C–C at ring); 2000–1650 cm^{-1} (harmonic bands). Meanwhile, these bands were not present in HN1 oil spectrum, pointing that the latter presented a structure predominantly aliphatic, which are in accordance with suppliers data (Table III). This

feature suggests that HN1 initially seems to be the best oil to fit the regulations.

The absence of bands at 1566 and 1641 cm^{-1} (axial deformation of C=C coupled with axial deformation of adjacent C–C bonds) indicated that cyclic alkenes structures were not detected in the oils. Moreover, the absence of bands in 1754 and 1786 cm^{-1} ($-\text{CH}=\text{CR}_2$ and $-\text{CR}=\text{CR}_2$, respectively, where R = halogen) shows that the technique did not detect the presence of halogen heteroatom in the oils.²⁴

Figure 3 shows FTIR spectra of SBR compositions. The following bands can be observed: 3072–3000 cm^{-1} (aromatic C–H stretching vibration); 3000–2840 cm^{-1} (aliphatic C–H stretching vibrations); 1667–1640 cm^{-1} (C=C stretching vibrations of the *cis*, *trans* $-\text{CH}=\text{CH}-$ and vinyl $-\text{CH}=\text{CH}_2$); 1600 cm^{-1} (aromatic and conjugated diene C=C stretching vibration); 1440–1437 cm^{-1} (aromatic C=C stretching vibration); 1000–694 cm^{-1} (angular deformation out of plane of C–H for *cis*, *trans* $\text{R}-\text{CH}=\text{CH}-\text{R}'$ and vinyl $\text{R}-\text{CH}=\text{CH}_2$); and 620 cm^{-1} (C=C–H twisting vibration).^{24–31} SBR compositions spectra did not exhibit marked differences, which indicates that the influence of different oils were not evident.

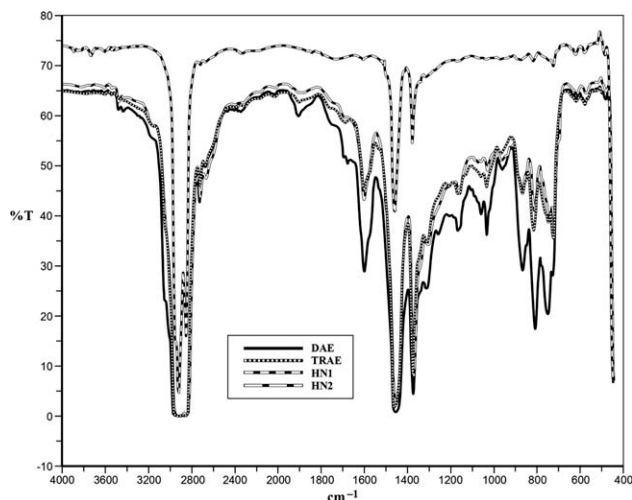


Figure 2 FTIR spectra of the crude oils.

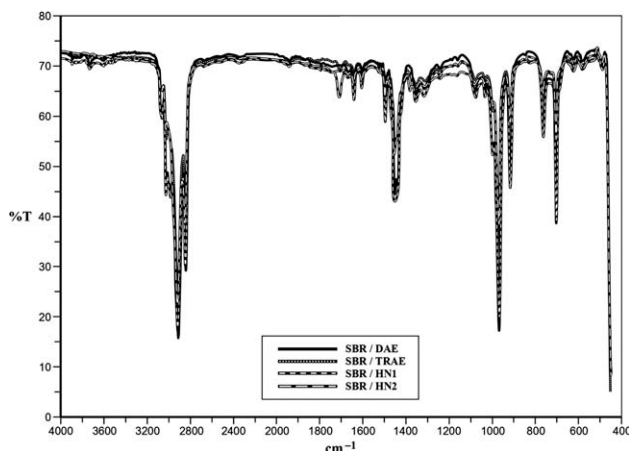


Figure 3 FTIR spectra of SBR compositions.

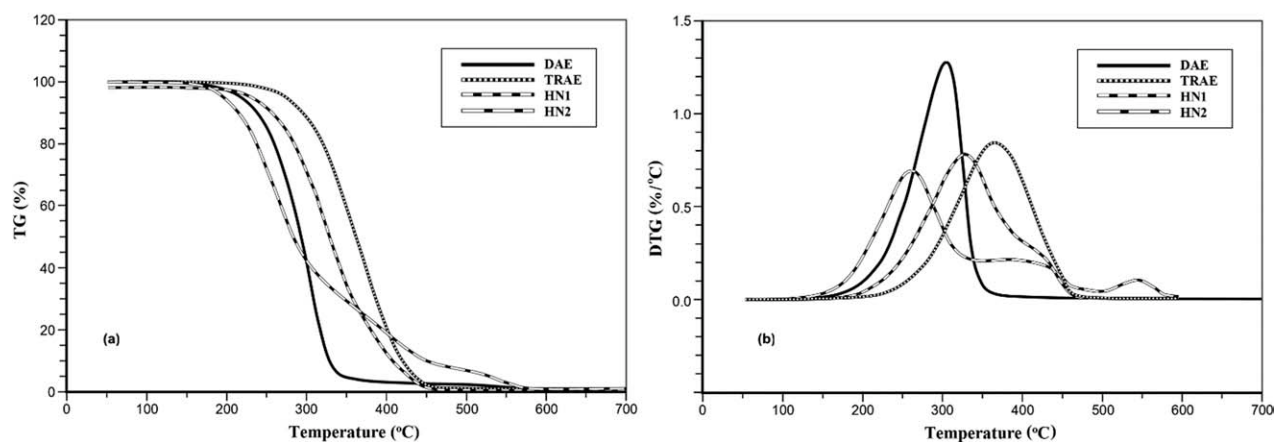


Figure 4 TG (a) and DTG (b) curves of crude oils.

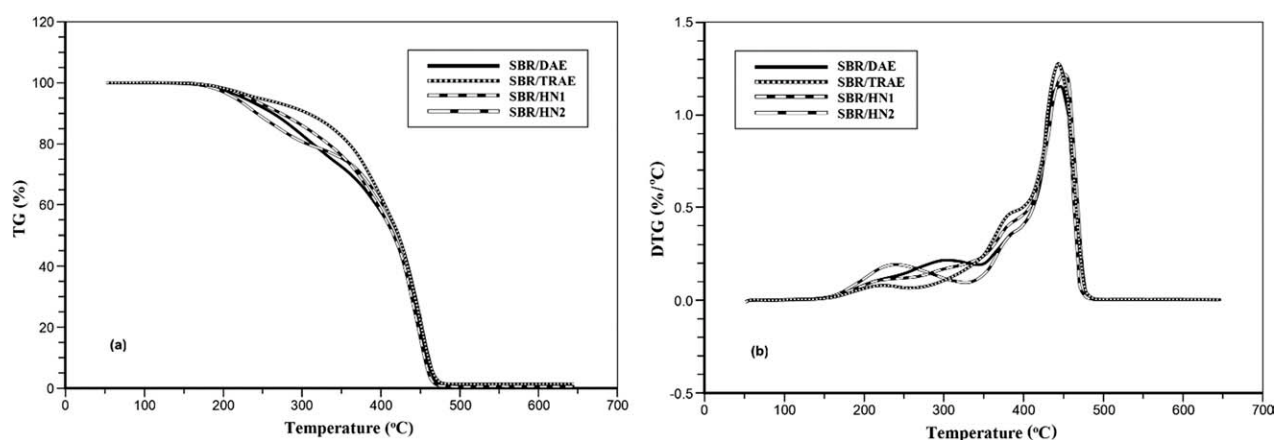


Figure 5 TG (a) and DTG (b) curves of SBR compositions.

Thermogravimetric analysis (TG)

The TG and DTG curves profiles of the crude oils and SBR compositions after vulcanization are presented in Figures 4 and 5, respectively. Table IV shows the thermogravimetric parameters obtained from the curves.

Usually, at low-heating rates, the degradation process results in differential weight loss (DTG) curves with several peaks, which indicates the complexity of the degradation generally not detected in weight loss (TG) curves. Thus, the derivative thermogravimetric curve (DTG) facilitates the observation of degradation stages of materials that may not be observed in TG curve.^{30,32,33}

The TG degradation curves of the oils showed mainly one-step profile whereas DTG curves for HN1 and HN2 detected more steps in the evolution of the degradation profile. Table IV shows the temperatures obtained from the curves. Since all oils are basically composed of hydrocarbons, it is possible that these differences are due to the presence of contaminants or heteroatoms, since all oils may contain

a small percentage of elements such as sulfur, nitrogen and oxygen.¹⁴

SBR is an elastomer that presents high filler-loading capacity and flex, crack-initiation and abrasion resistance. However, like other unsaturated rubbers,

TABLE IV
Thermogravimetric Data Obtained for the Samples

Samples	T_{onset}^a (°C)	$T_{1 \text{ max}}^b$ (°C)	$T_{2 \text{ max}}^b$ (°C)	$T_{3 \text{ max}}^b$ (°C)
Crude oils				
DAE	139	303	–	–
TRAE	189	364	–	–
HN1	172	324	425	–
HN2	137	260	410	538
SBR 1712 compositions				
SBR/DAE	175/369	297	380	444
SBR/TRAE	176/290	220	381	445
SBR/HN1	177	210	379	440
SBR/HN2	174/350	233	383	452

^aInitial temperature of degradation.

^bTemperature at maximum rate of weight loss in the corresponding step.

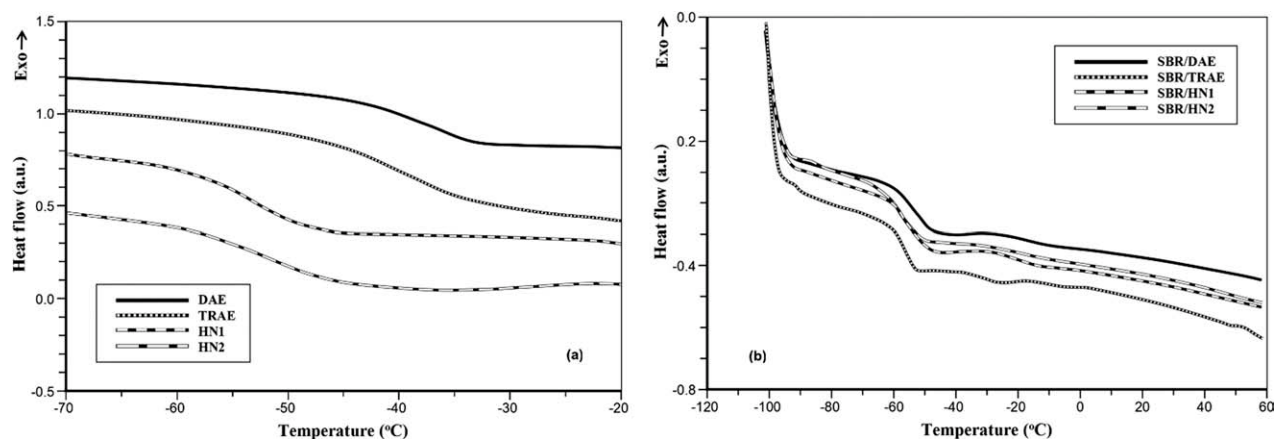


Figure 6 DSC curves obtained for (a) crude oils and (b) SBR compositions.

their thermal and ageing resistances are poor, due to the unsaturation in the butadiene segment.³⁴ According to Figure 5 and Table IV, the thermal degradation temperature of SBR compositions were almost the same. The loss of mass started at about 175°C. Two subtle steps were observed in all decomposition profile samples^{30,34} except for that in which HN1 oil was present.

On the other hand, it was found that the derivatives curves (DTG) showed more than two degradation stages for all compositions. According to literature, the volatilization of lower molecular weight materials (oils and additives) may occur between 250 and 350°C.²⁸ The values shown in DTG curves of the oils suggest their influence in the first step of degradation observed for SBR compositions. The second stage observed in DTG curves ($T_{2 \text{ max}}$ at about 380°C) can be related to depolymerization of segments from butadiene. The intense peak ($T_{3 \text{ max}}$ at about 445°C) was resultant from the degradation of butadiene and styrene.^{30,34}

Although the TG and DTG profiles of crude oils were significantly different, they promoted only slightly changes in the degradation profile of SBR as a whole and did not affect the thermal resistance of the rubber.

TABLE V
Glass Transition Temperature (T_g) of the Samples

Samples	T_g (°C)
Crude oils	
DAE	-39
TRAE	-41
HN1	-53
HN2	-52
SBR compositions	
SBR/DAE	-54
SBR/TRAE	-56
SBR/HN1	-57
SBR/HN2	-58

Differential scanning calorimetry (DSC)

Figure 6 presents the glass transition profiles of the crude oils (a) and SBR compositions (b) and Table V show their respective values.

DSC has been employed to study primary and secondary order transitions of oils and waxes.³⁵ The values obtained for the crude oils studied in this work were in accordance with those informed by the suppliers (Table III).²³ Aromatic rings promote more rigidity to the structures and elevate the transition temperature, which were observed for DAE and TRAE, whereas HN1 and HN2, in which paraffinic segments are present in higher contents, showed lower and similar glass transition temperatures.

Nevertheless, the T_g values obtained for SBR compositions were not markedly influenced by the type of extender oil employed. All compositions presented T_g values³⁴ varying in a narrow range.

Mechanical properties

Some mechanical properties of SBR compositions were determined and the results are depicted in Figures 7–10.

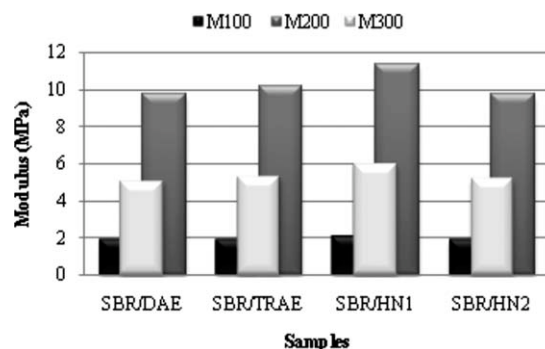


Figure 7 Young's modulus at 100%, 200% and 300% of SBR compositions (% error: -0.12).

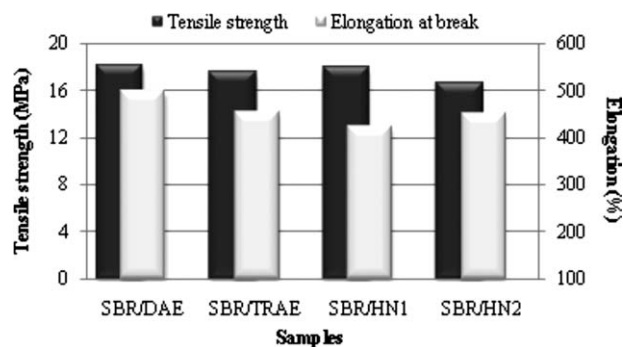


Figure 8 Tensile strength and elongation at break of SBR compositions (% error: tensile strength = 0.49%; elongation = -0.12).

SBR rubber has great compatibility with the aromatic oil, DAE, because in both hydrocarbon structures, there is the presence of aromatic rings, thereby promoting high hardness and mechanical resistance to the material. Emphasizing that, Table III shows that DAE oil contains the highest percentage of aromatic carbons (45%). It would be expected that extension oils with lower contents of PAHs resulted in reductions in the values of Young’s modulus, tensile strength, tear resistance, hardness, and abrasion of SBR compositions. On the other hand, elongation at break, and resilience should increase.²⁸ Despite of that, the safe oils tested in this work did not cause marked variations in any of these properties, when compared with the standard commercial formulation based on DAE. All formulations presented variations within the range of values required by tire manufacturers, indicating that any of the oils tested fulfill the demands. Taking all this into account, the choice of HN1, which presents the lowest content of aromatic carbons, seems to be the most suitable and the best possibility.

CONCLUSIONS

The substitution of DAE by any of the safe oils studied in this work seems to be possible without loss in

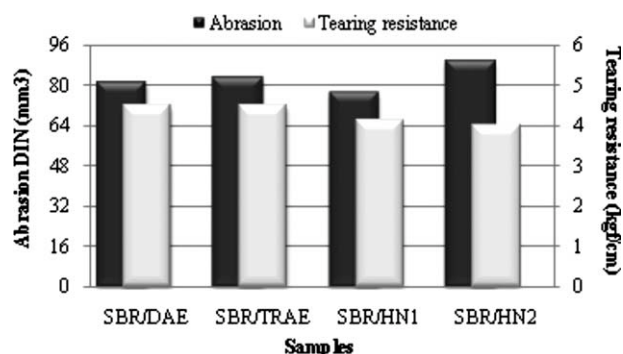


Figure 9 Abrasion loss and tearing resistance of SBR compositions (% error: abrasion: unknown; tearing resistance = 0.49).

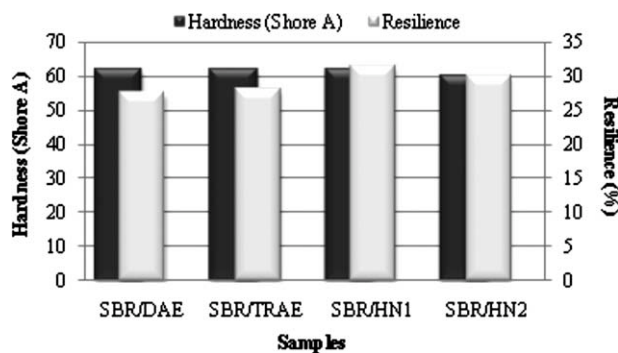


Figure 10 Shore A hardness and resilience of SBR compositions (% error: unknown).

thermal and mechanical properties of SBR 1712 compositions. There were not observed significant variations in thermal resistance, glass transition temperature, tensile parameters, tear and abrasion resistance, hardness, and resilience. All the characterization methods, including FTIR spectra of the compositions, produced similar profiles and results, the latter varying in very narrow ranges. Thereby, HN1, with the lowest aromatic carbon content, evinced to be the best among the safe oils tested.

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