

TG/FT-IR characterization of additives typically employed in EPDM formulations

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Abstract

Thermogravimetric analysis coupled to Fourier transform infrared spectroscopy (TG/FT-IR) is a very popular technique for rubbers characterization. It involves analyses of the base polymer and additives. Ethylene-propylene-diene (EPDM) rubbers are frequently investigated by TG/FT-IR; however, the focus has been the degradation temperature range of the polymer. In this study, unvulcanized and vulcanized EPDM rubber and its additives were investigated by TG/FT-IR, without solvent extraction, and in a wide temperature range. Initially, the additives were individually characterized. TG/FT-IR identified the characteristic groups of all the additives analyzed and distinguished them from each other. Afterwards, unvulcanized and vulcanized EPDM rubbers were investigated without prior extraction. TG/FT-IR detected absorptions due to the additives tetramethylthiuram monosulfide and 2-mercaptobenzothiazole. Both of these sulfur-containing additives were present in the EPDM formulation at concentrations of 0.7 phr (0.63 wt %). The TG/FT-IR technique had some limitations, because not all the additives in EPDM rubber were detected. Paraffin oil, stearic acid and 2,2,4-trimethyl-1,2-dihydroquinoline functional groups were not observed in either the unvulcanized or vulcanized EPDM. Nevertheless, in addition to the ability of this method to detect sulfur-containing groups, the lack of a pre-extraction reduces the time and effort required for additive analysis in rubbers.

Keywords: EPDM, additives, characterization, TG/FT-IR, TMTM, MBT.

1. Introduction

Additives are selected and incorporated into rubbers to provide specific properties. Useful rubbers can only be obtained by appropriate compounding. Some chemicals provide processing aid, extended shelf-life or improved long-term performance, others enhance polymer properties. As a result, rubbers are complex chemical materials, which are difficult to analyze^[1]. Analytical techniques that enable the detection of additives are of great importance for industries, especially for those cases in which they are present in very low concentrations.

Typically, there are two approaches for additive analysis in rubbers: extraction with solvent prior to analysis or direct determination. Extraction procedures can be very complex, labor-intensive, and not always reproducible^[1-3]; thus, direct analysis is always preferred if it is feasible.

Among the techniques for direct determination, thermogravimetric analysis coupled with Fourier transform infrared spectroscopy (TG/FT-IR) is one of the most powerful methods to study the thermal degradation of polymers. This technique has the merit of identifying the evolved gases of a polymer at different degradation temperatures; thus, it allows a temperature selective analysis^[4].

Ethylene-propylene-diene copolymer (EPDM) is one of the most important rubbers, and has uses in diverse applications, even in the aerospace field. Its saturated backbone provides remarkable resistance to oxygen, ozone, and heat^[5]. Some recently published studies have been related to the TG/FT-IR analysis of additives in EPDM. Jiang et al.^[6] used

TG/FT-IR to evaluate the effect of polyphenylsilsesquioxane (PPSQ) on the release of volatile products in EPDM samples. The results indicated that PPSQ affects volatile products of EPDM and is detected in its formulation by TG/FT-IR. Çavdar et al.^[7] studied different vulcanizing agent contents by TG/FT-IR. They observed that increasing vulcanizing agent content decreased band intensities of CO and CO₂ and enhanced the thermal stability of EPDM rubber. Özdemir^[8] utilized TG/FT-IR to evaluate irradiated EPDM rubber vulcanized with two types of peroxides. The main absorptions of this irradiated rubber were attributed to aromatic C-H, methylene C-H, methyl ether C-H, methyl C-H, CO, and CO₂. However, none of the studies attempted to detect additives at degradation temperatures other than the EPDM polymer degradation temperature.

In a previous study^[9], we employed Fourier transform infrared spectroscopy of gaseous pyrolyzates (PY-G/FT-IR) for the detection of additives in EPDM rubber. The absorptions of additives were identified in unvulcanized and vulcanized EPDM samples without prior extraction with solvent. This technique was able to detect sulfur-containing additives at concentrations as low as 1.4 phr (1.26%). However, as the whole amount of the evolved gas from pyrolysis was trapped into a gas cell at once, a temperature selective analysis was not possible.

A temperature selective analysis can be performed using TG/FT-IR; moreover, this technique can cover a wide range of temperatures and provide information related

to evolving products. Hence, this study is aimed at the detection of additives in EPDM rubber using TG/FT-IR without solvent extraction. Initially, each additive was individually characterized to identify its characteristic absorptions. Subsequently, unvulcanized and vulcanized EPDM samples were evaluated using raw EPDM rubber as a reference sample. The absorptions related to additives were identified by comparing the TG/FT-IR spectra of additives and EPDM samples.

2. Materials and Methods

2.1 Materials

Paraffin oil, stearic acid, 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ), tetramethylthiuram monosulfide (TMTM), and 2-mercaptobenzothiazole (MBT) were provided by Zanaflex Borrachas Ltda, Brazil, and analyzed individually as received.

As a reference sample, commercial grade EPDM Keltan 21 containing the diene ENB (ethylidene norbornene) was purchased from DSM Elastômeros do Brasil Ltda, Brazil, and used as received.

Unvulcanized and vulcanized (terminology in accordance with the ASTM D1566-11^[10]) samples were prepared using EPDM Keltan 21 and rubber-grade chemicals according to the composition listed in Table 1.

The molecular structures of the analyzed compounds prior to degradation are shown in Figure 1. MBT is represented by two different structures because this additive can be present in two tautomeric forms (Figures 1v and 1vi)^[11-13]. Contini et al.^[12] stated that MBT exists in the vapor phase only in its tautomeric thione (benzothiazoline-2-thione) form, which contains a C=S bond and a hydrogen bonded to the nitrogen, rather than the thiol form, which contains an endocyclic C=N bond and a hydrogen bonded to sulfur. According to Wu et al.^[13] and Mohamed et al.^[14], thione is the dominant form in the solid state. For a better understanding of the structural differences, the thione form of the MBT molecule is shown in Figure 1.

2.2 TG/FT-IR analysis

TG/FT-IR analyses were performed using a PerkinElmer Pyris 1 TGA coupled with a PerkinElmer Spectrum One FT-IR. The transfer line and FT-IR gas cell were maintained at 210 and 230 °C, respectively. The spectra were collected at resolution of 8 cm⁻¹ with a co-add of 8 scans per spectrum, resulting in one spectrum collected every 22 s. Each sample (ca. 20 mg) was heated from room temperature to 900 °C under a nitrogen atmosphere.

Heating rate and gas flow are the experimental parameters that have the greatest effect on the results of a TG/FT-IR experiment^[15]. Based on previous studies and recommendations of the manufacturer of the equipment, tests were performed to determine the optimal settings. Moreover, Gram-Schmidt reconstruction (GSR) profiles, which indicate the relative intensities of gases in the gas cell, were qualitatively compared. The optimal conditions, which maximized the FT-IR response, were determined to be the combination of a 20 °C/min heating rate with a 25 ml/min gas flow. According to Berbenni et al.^[15], a

well-adjusted TG/FT-IR experiment will present GSR and differential thermogravimetric (DTG) curves with similar profiles. In addition to providing the most intense absorptions, the selected parameters also showed excellent agreement between the GSR and DTG curves.

2.3 Selection of FT-IR spectra

In a typical TG/DTG result, the maximum value of the derivative curve indicates the maximum degradation rate. At this value, the quantity of evolving gases reaches its maximum. A single TG/DTG experiment can present one or multiple maxima depending on the sample components and its degradation characteristics.

An FT-IR spectrum was collected for each observed maximum degradation rate, which agreed with the maxima of the GSR profile with a delay of a few seconds. For some samples, a single spectrum was sufficient to represent the whole experiment, whereas for other samples, in which more than one degradation event was detected, more spectra were collected.

Moreover, the main absorptions determined in the spectra of additives were investigated in unvulcanized and vulcanized EPDM samples at the same temperature at which they appeared in the degradation of the additives.

Table 1. Composition of EPDM rubber (partially reproduced from Sanches et al.^[9]).

Component	Unvulcanized and Vulcanized (phr ^a)
EPDM Keltan 21	100
Paraffin oil	1.0
Stearic acid	0.5
TMQ (2,2,4-trimethyl-1,2-dihydroquinoline)	1.0
TMTM (tetramethylthiuram monosulfide)	0.7
MBT (2-mercaptobenzothiazole)	0.7
ZnO (zinc oxide)	2.0
Carbon black	5.0
S (sulfur)	0.7

^a parts per hundred parts of rubber.

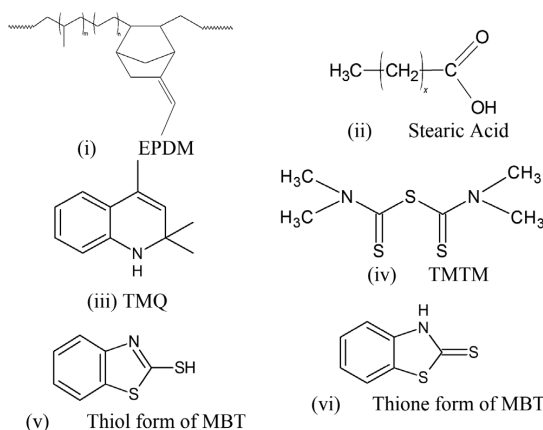


Figure 1. Molecular structure of the analyzed compounds prior to degradation (adapted from Sanches et al.^[9]).

In this study, all the FT-IR spectra were obtained from TG/FT-IR experiments, which are referred to as TG/FT-IR spectra.

3. Results and Discussion

3.1 Degradation temperatures

Initially, the additives, raw EPDM, and both unvulcanized and vulcanized EPDM were analyzed separately by TG/FT-IR. A set of TG/DTG curves, GSR curves, and FT-IR spectra was obtained for each sample.

Figure 2 shows the degradation temperatures obtained from the TG/DTG curves. A comparison between the degradation ranges of EPDM and its additives is useful because it indicates the temperature at which the characteristic absorptions of the additives should be searched for in the unvulcanized and vulcanized EPDM TG/FT-IR experiments.

Figure 2 shows that only TMTM presents a narrow degradation temperature region of 180-310 °C, whereas the other additives show wide degradation regions. Raw EPDM degradation starts at approximately 250 °C; therefore, at lower temperatures, additive absorptions should be observed in unvulcanized and vulcanized EPDM without interference from characteristic EPDM bands. At higher temperatures, most additive absorptions should simultaneously be observed with the polymer bands.

The comparison between raw, unvulcanized and vulcanized EPDM confirm their peculiarities. Raw EPDM presents a more narrow temperature degradation range, as expected for a neat polymer. Unvulcanized and vulcanized EPDM degradation is broader because of the additive content. The comparison between unvulcanized and vulcanized EPDM shows that unvulcanized EPDM degradation begins at a lower temperature, although both contain the same formulation. Vulcanized EPDM was heated

to approximately 150-180 °C in the crosslinking process; therefore, to some extent, it loses a certain quantity of low molecular weight additives.

3.2 TG/FT-IR analysis of additives

IR spectra of gaseous products can be very complex because they present a large number of absorptions. In this study, for peak assignment, the presence or absence of characteristic functional groups in the TG/FT-IR spectra was used. Figure 3 shows the FT-IR spectra of additives obtained from the TG/FT-IR technique.

The main bands observed in the TG/FT-IR spectrum of paraffin oil (Figure 3a) are 3085, 3016, 2933, 2868, 1462, 1380, 949, and 911 cm^{-1} . The peaks at 3085 and 3016 cm^{-1} are assigned to the C-H group and/or C-H aromatic group, whereas those at 2933, 2868 and 1380 cm^{-1} are assigned to the CH_3 group. The band at 1462 cm^{-1} is assigned to C-H group. Although aromatic groups are not expected in the TG/FT-IR spectrum of paraffin oil, its presence can be explained by the fact that rubber-grade paraffin oils may contain 26%-40% of naphthenic oil and 2%-7% of aromatic oil^[16].

The TG/FT-IR spectrum of stearic acid is shown in Figure 3b. The band at 3576 cm^{-1} is assigned to the OH group. The peaks at 2933 and 2864 cm^{-1} are assigned to the CH_2 groups. The absorption at 1776 cm^{-1} is assigned to the $\text{C}=\text{O}$ group. The bands at 1462 and 1126 cm^{-1} are assigned to the CH_2 group, whereas the band at 1372 cm^{-1} is assigned to the CH_3 group^[17,18].

The TG/FT-IR spectra corresponding to TMQ degradation at 362 and 473 °C are shown in Figures 3c and 3d, respectively. The spectrum at 362 °C showed a band at 3015 cm^{-1} , which is assigned to the C-H or H-C=C group. The bands around 2968-2877 and 1059-1005 cm^{-1} are assigned to the CH_3 group. The peaks at 1603 and 744 cm^{-1} are assigned to the

Component/ Temperature Range	25-100 °C	100-200 °C	200-300 °C	300-400 °C	400-500 °C	500-600 °C	600-700 °C	700-800 °C	800-900 °C
Paraffin oil			—————						
Stearic acid		—————							
TMQ		—————							
TMTM		—————							
MBT		—————							
Raw EPDM			—————						
Unvulcanized EPDM		—————							
Vulcanized EPDM		—————							

Figure 2. Degradation temperature of components from TG/FT-IR experiments.

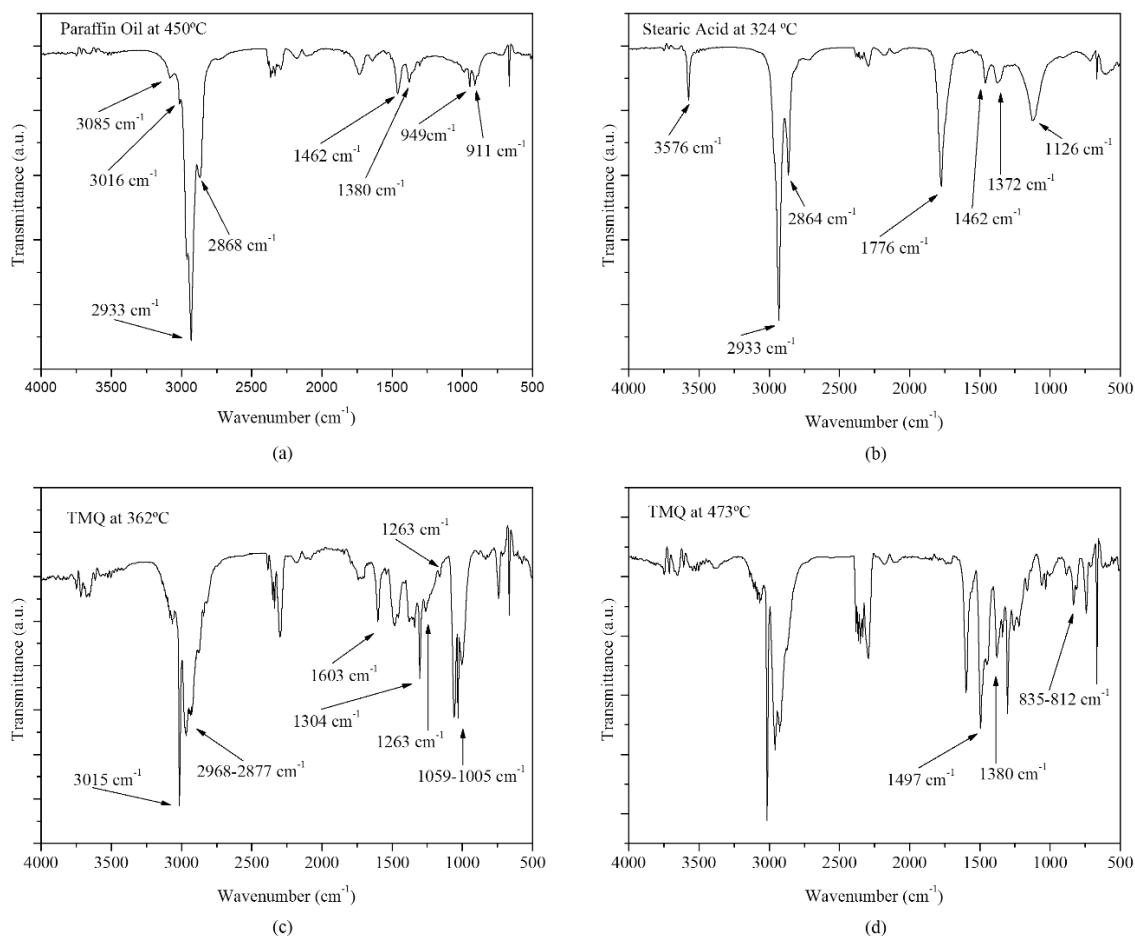


Figure 3. TG/FT-IR spectra of (a) paraffin oil at 450 °C; (b) stearic acid at 324 °C; (c) TMQ at 362 °C; and (d) TMQ at 473 °C.

C-C aromatic and C-H groups, respectively. The absorption at 1304 cm^{-1} is assigned to the N-H^[19] and/or C-N^[20] groups, whereas the bands at 1263 and 1162 cm^{-1} are assigned to the C-N aromatic group.

The spectrum at 473 °C showed the same bands as the one at 362 °C; however, other absorptions were detected, which are described as follows. The bands at 1497, 1380, and 835-812 cm^{-1} are assigned to the C-C aromatic and/or CHN, CH₃, and C-H groups of the benzene ring, respectively^[20]. These bands were possibly not detected at 362 °C because of the low amount of evolved gas at this temperature.

Figure 4a shows the TG/FT-IR spectrum of TMTM at 294 °C. The bands at 2941-2812 cm^{-1} are assigned to the CH₃ group. The bands at 2072 and 2048 cm^{-1} probably can be assigned to the N=C=S (isothiocyanate) group^[21-24].

The spectra of CS₂ in the gaseous state obtained from the reference databases^[25,26], show absorptions at approximately 2320, 2179, and 1530 cm^{-1} , which are in excellent agreement with the bands observed at 2336-2316, 2193-2179, and 1539-1524 cm^{-1} . Moreover, similar to other studies, a band located between 1523 and 1541 cm^{-1} can be attributed to the CS₂ group^[27,28].

Therefore, considering the chemical structure of TMTM and the references in the literature, doublets can be attributed to the presence of the C=S and/or CS₂ group in the TMTM degradation products.

The TG/FT-IR spectra corresponding to MBT degradation at 361 and 784 °C are shown in Figures 4b and 4c, respectively. The spectrum at 361 °C has a band at 3748 cm^{-1} , which can be assigned to the N-H group. The peaks at 3076 and 755 cm^{-1} are assigned to the aromatic C-H group. The band at 2895 cm^{-1} is assigned to the CH₂ group. The doublet at 2071-2046 cm^{-1} and the peak at 656 cm^{-1} are assigned to the N=C=S group^[20]. These absorptions are in excellent agreement with the benzothiazole spectrum in the literature^[25]. Doublets at 2193-2179 (very subtle) and 1539-1525 cm^{-1} are assigned to the C=S and/or CS₂ group, which is analogous to the TMTM assignment. These assignments confirm the presence of the thione form in the vapor phase, as indicated by Contini et al.^[12].

After 450 °C, the intensity of the bands observed in the 361 °C spectrum starts decreasing with the emergence of a doublet at 1376-1343 cm^{-1} , indicating the structural transformation of the molecule. The spectrum at 784 °C shows this doublet; however, it is inconclusive for determining the evolved products during MBT thermal degradation.

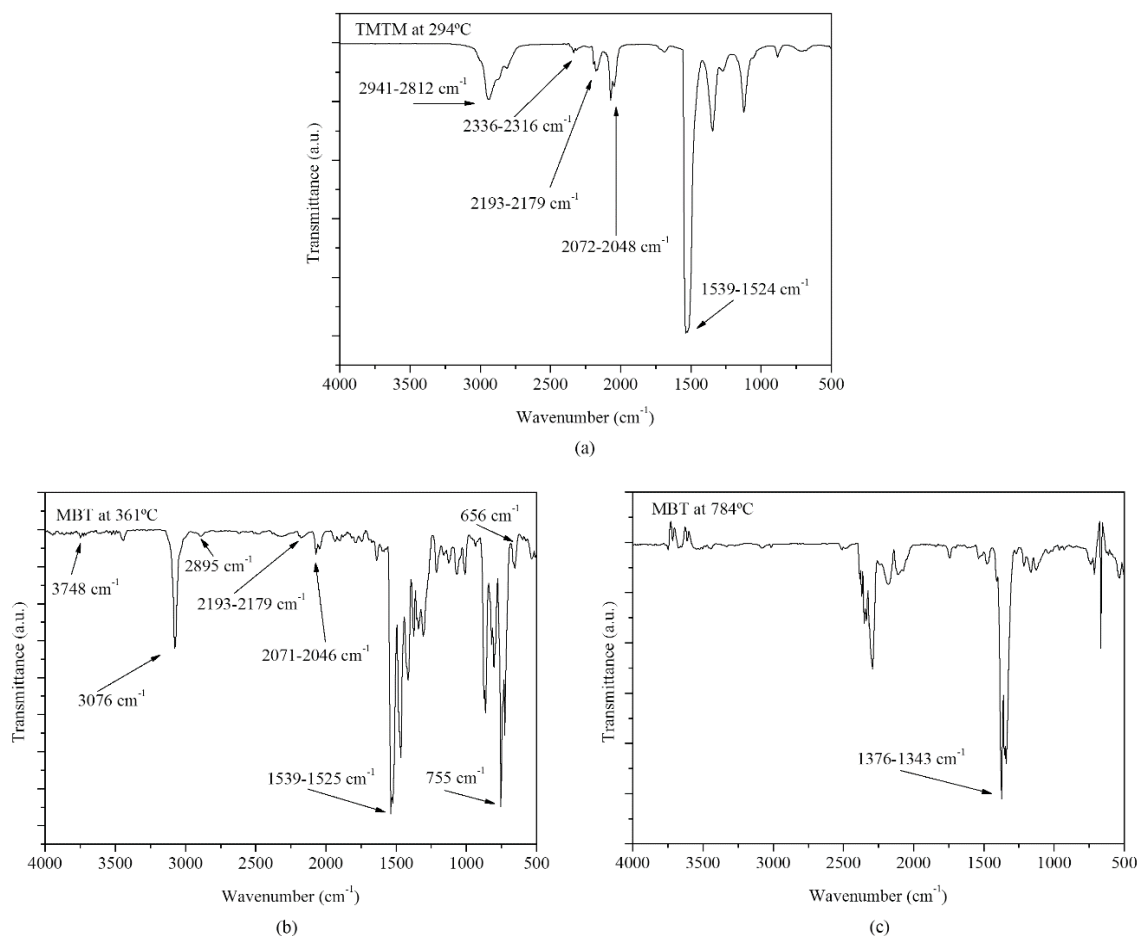


Figure 4. TG/FT-IR of (a) TMTM at 294 °C; (b) MBT at 361 °C; and (c) MBT at 784 °C.

According to Brooks et al.^[29], pyrolysis of pure benzene leads to ring opening at 763 °C, leading to the generation of methane as one of the degradation products. The spectrum of methane from the literature^[25] shows absorptions in the region of 1376-1343 cm^{-1} , indicating that they could be related to the CH_3 group. Nevertheless, recent studies have assigned these peaks to the C-C group of the benzene ring^[30,31], or to the ring vibrations of the heterocyclic MBT ring^[21].

3.3 TG/FT-IR analysis of EPDM

TG/FT-IR results of raw, unvulcanized, and vulcanized EPDM can complement each other. In this study, raw rubber was analyzed as a reference sample, and its FT-IR spectrum was compared with the spectra of unvulcanized and vulcanized EPDM to differentiate the polymer absorptions. Unvulcanized rubber was analyzed by TG/FT-IR to obtain the spectrum before vulcanization, which is when additives are chemically preserved.

The TG/FT-IR spectra of the evolved products of raw, unvulcanized, and vulcanized EPDM are shown in Figure 5. Figure 5a shows the TG/FT-IR spectrum of raw EPDM. The peak at 3086 cm^{-1} is assigned to the olefinic and/or aromatic C-H. The peaks at 988 and 911 cm^{-1} are assigned to the vinylic C=C. The band around 949 cm^{-1} is assigned

to the trans C=C. The bands observed at 889 cm^{-1} and at 1385 cm^{-1} are assigned to the $\text{RR}'\text{CCH}_2$ and CH_3 groups, respectively^[20]. The absorptions detected in the raw EPDM FT-IR spectrum can help evaluate additive-related absorptions in the formulated EPDM.

TG/FT-IR spectra of unvulcanized and vulcanized EPDM (Figures 5b and 5c) are very similar at 272 and 280 °C, respectively. These spectra show very weak doublets around 2192-2179 and 2071-2047 cm^{-1} . A more intense doublet is detected in the region of 1540-1525 cm^{-1} . These peaks are absent in the spectrum of raw EPDM (Figure 5a); thus, they are related to the additives. Only TMTM and MBT TG/FT-IR spectra show similar bands; thus, it can be assumed that these absorptions are related to them.

Figures 5d and 5e show the TG/FT-IR spectra of unvulcanized and vulcanized EPDM at 509 and 517 °C, respectively. At these temperatures, unvulcanized and vulcanized EPDM degradation products show only polymer-related absorptions, which are in excellent agreement with the raw EPDM TG/FT-IR spectrum (Figure 5a).

TG/FT-IR results of raw EPDM, as well as the results for unvulcanized and vulcanized EPDM at 509 and 517 °C, respectively, exclusively show the EPDM polymer. Their assignments are in accordance with a published study^[32]

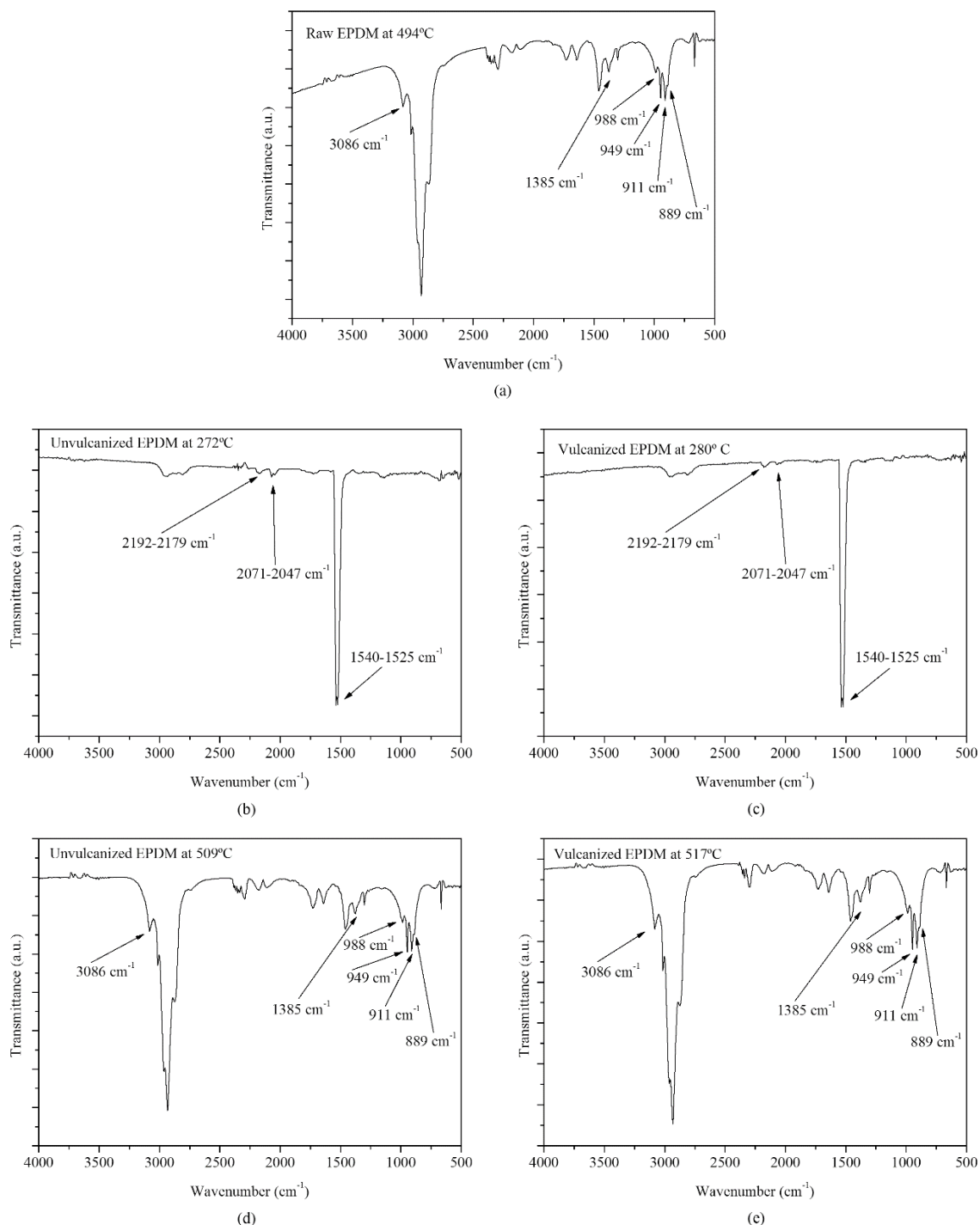


Figure 5. TG/FT-IR of (a) raw EPDM at 494 °C; (b) unvulcanized EPDM at 272 °C; (c) vulcanized EPDM at 280 °C; (d) unvulcanized EPDM at 509 °C; and (e) vulcanized.

that evaluated EPDM rubber by coupling pyrolysis–gas chromatography and mass spectrometry (PY-GC/MS). Its results indicate a mix of alkanes and alkenes among the major products of EPDM thermal degradation.

Moreover, the main absorptions of paraffin oil, stearic acid, and TMQ were investigated in EPDM TG/FT-IR spectra at the temperature range, in which the additive degradation

was observed. The TG/FT-IR spectra of unvulcanized and vulcanized EPDM show no peaks that could be related to these additives.

In a previous study^[9], a band at 771/772 cm^{-1} from paraffin oil, stearic acid, and TMQ pyrolysis was detected in the PY-G/FT-IR spectra of unvulcanized and vulcanized EPDM. In the TG/FT-IR experiments, the absence can be

explained by features of the technique. In this study, the evolved gases are carried to FT-IR by the flow gas, which dilutes the degradation products; moreover, the amount of sample is significantly less than the one analyzed with the PY-G/FT-IR technique.

Table 2 summarizes the functional groups assigned to the additives and EPDM by TG/FT-IR experiments, and relates them to the temperature at which spectra were collected. It can be seen that unvulcanized and vulcanized EPDM spectra were collected at a higher temperature than the raw EPDM spectrum. As the temperatures are related to the maximum degradation rate of the polymer, the differences are possibly

due to the additives (unvulcanized and vulcanized EPDM) and the crosslinking effect (vulcanized EPDM only).

Some differences in absorption intensities are expected between the TG/FT-IR spectra of unvulcanized and vulcanized EPDM. Vulcanized gaseous output is expected to be lower in quantity with less intense absorptions because the crosslinking process involves temperatures around 150 °C, which can alter the additives and cause chemical reactions. Although this study involves only qualitative analysis, this quantitative aspect could prevent detection of additives. For example, sulfur compounds could be partially or totally consumed in the reticulation reaction; consequently, their bands might lose intensity or even disappear from the

Table 2. Functional groups assigned in this study.

Component	Temperature	Wavenumber (cm ⁻¹)	Functional Groups assigned by TG/FT-IR
Paraffin Oil	450 °C	2933, 2968 and 1380	CH ₃
		3085 and 3016	CH and/or C-H aromatic
Stearic Acid	324 °C	1462	CH
		3576	OH
		2933 and 2864	CH ₂
		1776	C=O
		1462 and 1126	CH ₂
TMQ	362 °C	1372	CH ₃
		3015	C-H or H-C=C
		2968-2877 and 1059-1005	CH ₃
		1063	C-C aromatic
		744	C-H
	473 °C	1304	N-H and/or C-N
		1263 and 1162	C-N aromatic
		3015	C-H or H-C=C
		2968-2877 and 1059-1005	CH ₃
		1063	C-C aromatic
TMTM	294 °C	744	C-H
		1304	N-H and/or C-N
		1263 and 1162	C-N aromatic
		1380	CH ₃
		835-812	C-H of benzene ring
		2336-2316, 2193-2179 and 1539-1524	CS ₂ and/or C=S
MBT	361 °C	2941-2812	CH ₃
		2072 and 2048	N=C=S
		3748	N-H
		3076 and 755	C-H
		2895	CH ₂
Raw EPDM	494 °C	2071-2046 and 656	N=C=S
		2193-2179 and 1539-1525	CS ₂ and/or C=S
		1376-1343	CH ₃ or C-C aromatic or ring vibrations of the heterocyclic ring
Unvulcanized and vulcanized EPDM	272 and 280 °C, respectively	988 and 911	C=C vinyl
		949	C=C trans
		889	RR'CCH ₂
		1385	CH ₃
		3086	C-H olefinic and/or aromatic
Unvulcanized and vulcanized EPDM	509 and 517 °C, respectively	2192-2179, 2071-2047 and 1540-1525	CS ₂ and/or C=S
		Same wavenumbers as raw EPDM	Same absorptions as raw EPDM

FT-IR spectra of vulcanized rubber. Nevertheless, in this study, the unvulcanized and vulcanized EPDM TG/FT-IR spectra are very similar.

Intriguingly, the TG/FT-IR technique was able to detect only the sulfur-containing additives TMTM and MBT in unvulcanized and vulcanized EPDM. Both additives demonstrated similar characteristic absorptions related to sulfur compounds in the regions of 2192-2179, 2071-2047, and 1540-1524 cm^{-1} . These results confirm that absorptions related to the sulfur compounds show stronger intensities in the gaseous state than in the solid and liquid state^[9]. TG/FT-IR was capable of detecting sulfur compounds in concentrations as low as 1.4 phr (1.26%), considering the sum of TMTM and MBT content in the compounds. This confirms the potential of this method to investigate these types of materials, even with a considerably smaller sample than that used in the PY-G/FT-IR technique^[9].

In our former study^[9], the PY-G/FT-IR technique was unable to differentiate TMTM and MBT from each other; however, TG/FT-IR could easily distinguish between them. This demonstrates the superiority of TG/FT-IR for analyzing sulfur additives. In fact, PY-G/FT-IR and TG/FT-IR can complement each other because the former has the advantage of providing a very concentrated evolved gas, which can be helpful in analyzing additives whose products present weak absorptions or are present in low concentrations in the rubber compound. On the other hand, TG/FT-IR has the disadvantage of yielding gases diluted with the flow gas, but is able to provide spectra at different temperatures and thus differentiate the components of complex degradation samples.

4. Conclusion

TG/FT-IR characterization of additives frequently used in EPDM rubber was performed. This technique was capable of distinguishing all the additives from each other without exception. By analyzing the degradation of these additives at different temperatures, TG/FT-IR demonstrated very distinct spectra. Furthermore, TMTM and MBT accelerators showed some similar characteristic absorptions, which are related to sulfur compounds. The presence of these specific absorptions enables the differentiation of additives with and without sulfur, by TG/FT-IR.

This technique was able to detect absorptions of sulfur additives in EPDM rubber at concentrations as low as 1.4 phr (1.26%), even in vulcanized EPDM. These specific absorptions were detected at temperatures lower than the temperatures at which the polymer bands were observed, in accordance to TMTM and MBT degradation characteristics. Moreover, the identification of functional groups of these additives was possible without their prior extraction using solvents in both unvulcanized and vulcanized EPDM.

Therefore, the TG/FT-IR technique can be employed for the analysis of separate additives, neat rubber (raw), and unvulcanized and vulcanized compounds. It demonstrated temperature selectivity, enabling the investigation of specific temperatures at which the additives degrade. Although the technique was unable to detect paraffin oil, stearic acid, and TMQ additives in unvulcanized and vulcanized EPDM, the sulfur-related characteristic absorptions of TMTM and MBT were identified.

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