

THERMAL CHARACTERIZATION OF ASPHALT MIXTURES BY TG/DTG, DTA AND FTIR

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The quality of a road relies on the good use of the on road surface and its maintenance along the years. The technology used and the corrections contributes to the prevention of early road destructions. Pavement with polymer and others additives exhibits greater resistance to rutting, thermal cracking, and decreased fatigue damage, stripping and temperature susceptibility. Samples of CAP 40, SBS 440/02, L 1861/04, L 784/05 and L 2000/04 were analyzed by thermogravimetry (TG), derivative thermogravimetry (DTG), differential thermal analysis (DTA) and FTIR. Thermal characterizations showed that the main decomposition stage refers to asphaltenes and samples with additives exhibited a slight increase in thermal stability. The kinetic study, by Kissinger, showed that the sample with the highest stability was the SBS 440/02. Fourier transform infrared spectroscopy (FTIR) analysis suggested that these asphalt samples were originated from light oil.

Keywords: asphalt mixtures, thermal analysis

Introduction

Asphalt is responsible for the carpeting of almost all the pavements in cities worldwide. Processes of asphalt modification involving natural and synthetic polymers were patented as early as 1843. Projects were underway in Europe in the 1930s, and neoprene latex began to be used in North America in the 1950s. In the late 1970s, Europe was ahead of the United States in the use of modified asphalts because the European use of contractors, who provided warranties, motivated a greater interest in decreased life cycle costs, even at higher initial costs [1]. Nowadays the technology used and the corrections contributes to the prevention of early road damages. In this way, researches all around the globe have been studying the components and properties of the raw material for pavements. There are some publications about crude oil; its components, properties and performance. It is relevant to mention an interest study made by Kök [2] focusing on the kinetic study of crude oil. Also was informed that exist a correlation between activation energy and °API [3].

Asphalt cement from petroleum, CAP, is derived from the distillation of petroleum crude in a refinery. The chemistry and composition of crude is highly dependent upon its source. As a consequence of the variable nature of crude oil, asphalt cement contains a wide variety of different molecules with different polarity and molecular size making the chemical compo-

sition of asphalt cement exceedingly complex [4]. CAP being a complex mixture, whose main constituents are the asphaltenes, saturated compounds and aromatics as shown in Figs 1 and 2 [5]. Gonçalves *et al.* [6] made an important approach about thermal decomposition, confirming a formation of coke during the pyrolysis of asphaltenes. Asphaltenes are the most important asphalt constituent and the essential components with the largest average molecular mass among crude oils [7]. They are also a class of materials of considerable importance in the refinery processes, since their presence may hinder the thermal and catalytic transformation of petroleum residues [6]. The asphalt cements show some modification on its physical and chemical properties when submitted to a thermal oxidative process, therefore requiring the understanding of the effects of these new materials when added to asphalts. Asphalt cement may be modified by several different means including treatment with polyphosphoric acid or addition of polymers. Acid treatment is performed at the refinery while polymers are typically added at a terminal [4]. Synthetic polymer as styrene-butadiene-styrene (SBS) is a block copolymer that increases the elasticity of asphalt. It is probably the most appropriate polymer for asphalt modification, although the addition of SBS type block copolymers has both economic and serious technical limitations. Although low temperature flexibility is increased, some authors claim that a decrease in strength and resistance to pen-

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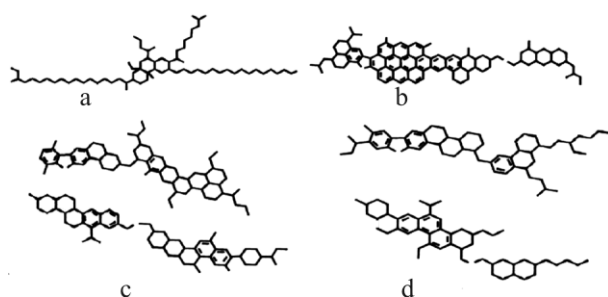
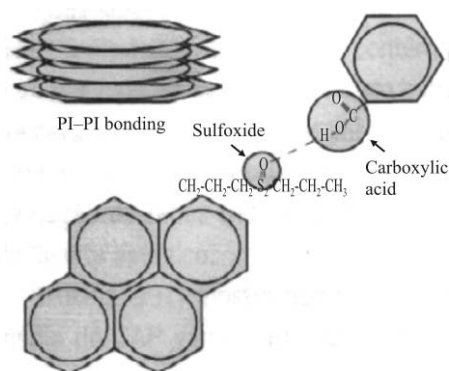
Table 1 Properties of asphalt samples [8]

Sample	Additives to asphalt (mass/mass%)	Density at 20/4°C (g mL ⁻¹)	Penetration at 25°C, 100 g/dmm	Melting point/°C	Viscosity 135°C/cP	Sulfur/%	SARA
CAP 40	n.a	1.06	30	n.a.	570	n.a.	n.a.
SBS 440/02	3% styrene butane styrene	1.07	52	51.4	720.8	n.a.	n.a.
L 1861/04	0.5% poly-phosphoric acid	1.03	66	50.6	356.7	0.94	n.a.
L 784/05	3% maleic anhydride	1.05	33	60.1	900	n.a.	10% saturates 40% aromatics 18% resin 32% asphaltenes
L 2000 /04	1% poly-phosphoric acid	1.03	102	46	233	0.932	n.a.

n.a.: not available

etration is observed at higher temperatures [1]. In this study [8], different mixtures were evaluated as showing in Table 1. Besides knowing the components and behavior of asphalts, it is important to study the kinetic of these oil derivatives. Kinetic data was necessary for a reliable performance prediction by using a model, such as Arrhenius method [9].

The aim of this research is to characterize by TG/DTG and DTA, and FTIR the different samples of asphalt mixtures comparing through a kinetic study their activation energy and thermal stability.

**Fig. 1** Representation of asphalt components: a – saturated, b – asphaltenes, c – aromatics and d – resins [5]**Fig. 2** Structure model of asphalt suggested by Strategic Highway Research Program [5]

Experimental

The asphalt samples used during the experiment was a CAP 40 (asphalt cement of petroleum pure), SBS 440/02 (cap with 3 mass/mass% SBS), L 1861/04 (cap with 0.5 mass/mass% polyphosphoric acid), L 784/05 (cap with 3 mass/mass% maleic anhydride), L 2000/04 (cap with 1 mass/mass% polyphosphoric acid). All samples were supplied by CENPES/Petrobras from Brazil.

Thermal analysis

All samples were evaluated by thermal analysis on a TA Instruments, model SDT 2960, under nitrogen atmosphere, sample mass around 5 mg, with heating rate of 10°C min⁻¹, heated from room temperature to 1000°C. The nitrogen flow during the experiments was 120 mL min⁻¹. The TG/DTG and DTA were performed at three different heating rates as 8, 10 and 12°C min⁻¹. All the experiments were performed three times for reproducibility.

Fourier transform infrared spectroscopy

Samples were also analyzed on a Spectrum one FTIR Spectrometer, (Perkin Elmer Co., Norwalk, CT, USA), from 4000 to 650 cm⁻¹ with ATR.

Results and discussion

Figure 3 shows TG, DTG and DTA curves for Brazilian asphalt sample, CAP 40, showing a decomposition stage on the TG, from 290 to 500°C, with mass loss of 80% suggesting the decomposition of asphaltenes to produce coke [6]. The DTG curve confirms one stage and the maximum mass loss rate at 460°C

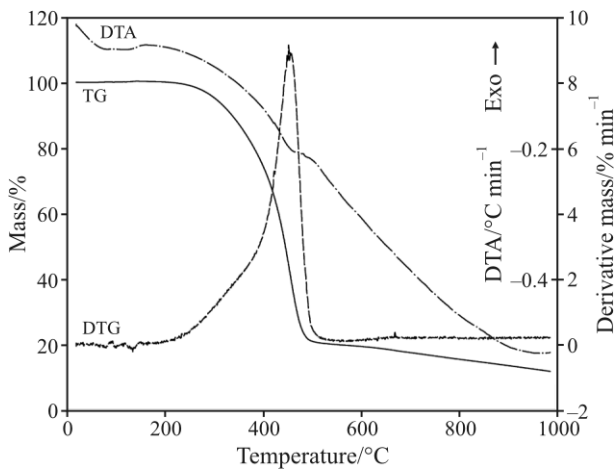


Fig. 3 TG/DTG/DTA curves for CAP 40 sample

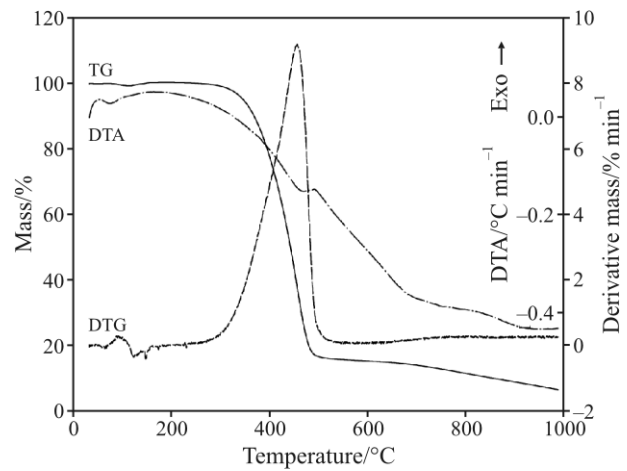


Fig. 5 TG/DTG/DTA curves for L 1861/04 sample

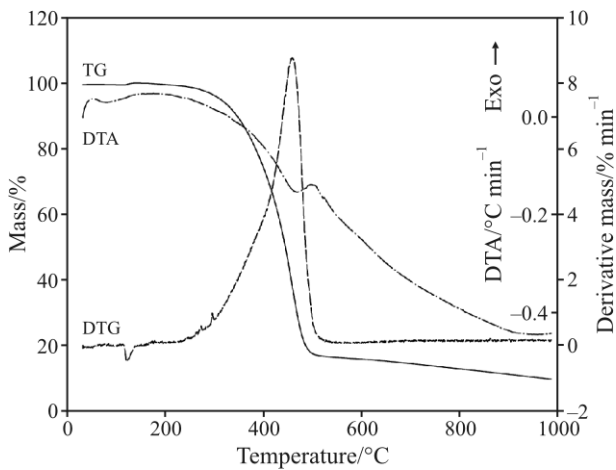


Fig. 4 TG/DTG/DTA curves for SBS 440/02 sample

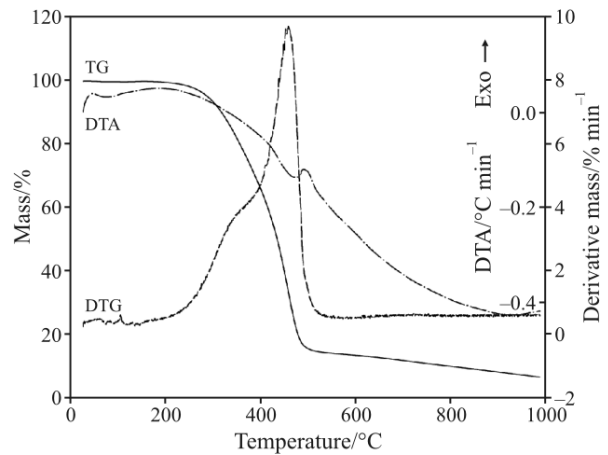


Fig. 6 TG/DTG/DTA curves for L 784/05 sample

and DTA curve reveals one endothermic event at around 460°C [10].

TG/DTG and DTA curves for asphalt sample SBS 440/02 (Fig. 4) showed one decomposition stage (DTG) at 462°C and one endothermic event at around 470°C on the DTA curve. This sample showed a very similar thermal behavior when compared to CAP 40.

Figure 5 presents L 1861/04 sample. TG curve showed one main stage of decomposition starting at 337 and ending at 500°C. DTG analysis had a mass loss rate at 450°C representing the decomposition of asphaltenes. The DTA curve showed one endothermic event at 470°C and another small event at around 830°C possibly showing the presence of coke.

Figure 6 exhibits thermogravimetric curve for asphalt L 784/05 sample, presenting one decomposition stage (281 to 500°C) but two decomposition stages were observed on the DTG curve, first at 350°C, which can be attributed to additives' evaporation (maleic anhydride) and the second one at 462°C, referring to the decomposition of asphaltenes. DTA

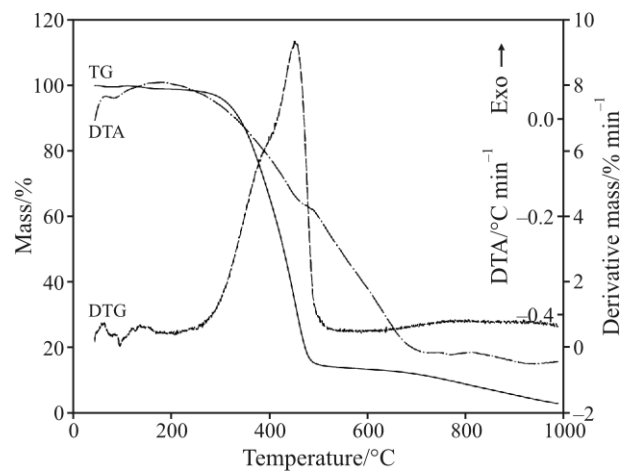


Fig. 7 TG/DTG/DTA curves for L 2000/04 sample

curve showed one endothermic event at 460°C, indicating the degradation of the asphaltenes.

Figure 7 shows TG, DTG and DTA curves for Brazilian asphalt sample, L 2000/04, which shows one decomposition stage on the TG, from 306 to

Table 2 Summary of TG/DTG properties results for the asphalt samples

Sample	Onset temp./°C	Maximum temp. decomp./°C	FTD/%	Mass loss/%	Residue at 1000°C/%
CAP 40	290	460	500	80	20
SBS 440/02	312	462	500	83	17
L 1861/04	337	450	500	83	17
L 784/05	281	462	500	86	14
L 2000/04	306	450	487	85	15

FTD: final temperature decomposition

487°C, with mass loss of 85%. The DTG curve shows one stage and the maximum mass loss rate at 450°C. DTA analysis presented a similar behavior to sample L 784/05.

Table 2 presents a summary of their results for thermal analysis (TG/DTG). It was interesting to observe that for all the samples mentioned a similar thermal behavior only in the maximum temperature decomposition was found, but different on the first decomposition stages and showed different amount on residue at 1000°C, suggesting inorganic compounds. It could be guessed that to add polymer such as: styrene butane styrene or reagents like: polyphosphoric acid and maleic anhydride in asphalts to obtain asphalt mixtures could bring an increase in their thermal stability. So for a better understanding of these results, it was made a preliminary kinetic study using Kissinger model [11].

In the course of this research, three heating rates were performed as shown in Figs 8–10. An evaluation of DTG curves was done by applying Kissinger model as shown in Table 3. Activation energy values indicated that the sample with SBS exhibited the higher value (120.29 kJ mol⁻¹), suggesting this asphalt mixture as the highest thermal stability. When

comparing with a kinetic study made by other authors [12, 13], in which was evaluated the activation energy of crude oil and crude oil mixtures; it is interesting mentioned that the values found for asphalt mixtures were superior than for crude oils, as expected.

Figure 11 exhibits a comparison with five samples of asphalts with different additives. These FTIR

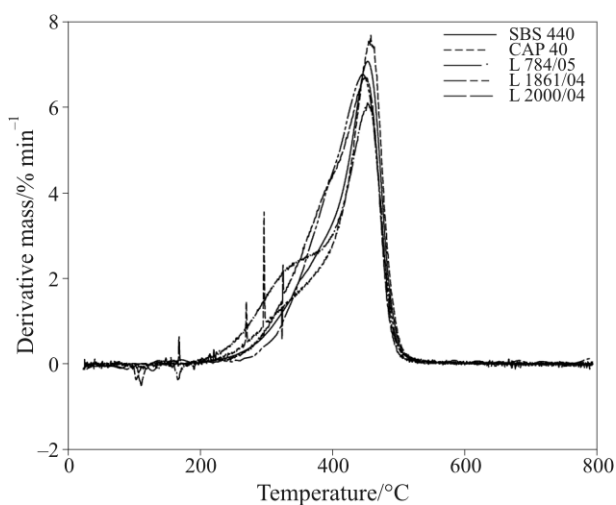
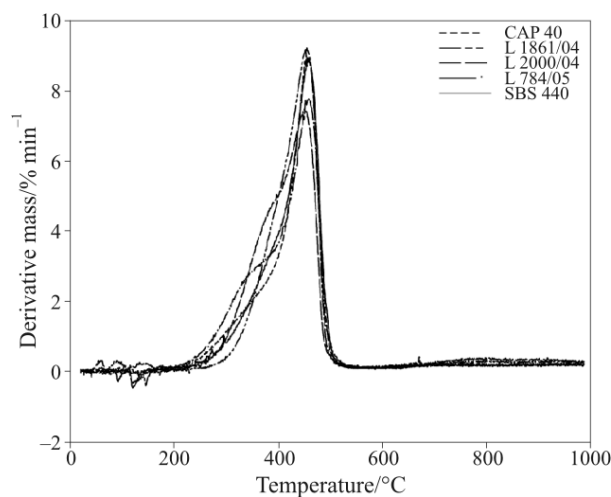
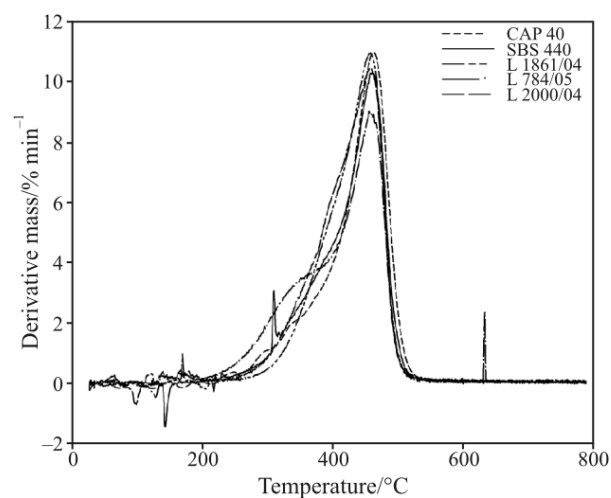
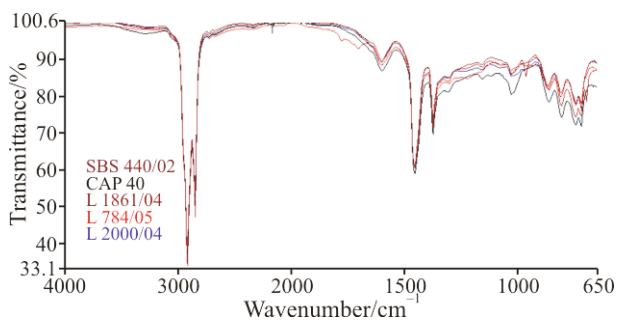
**Fig. 8** DTG curves for asphalt samples with heating rate of 8°C min⁻¹**Fig. 9** DTG curves for asphalt samples with heating rate of 10°C min⁻¹**Fig. 10** DTG curves for asphalt samples with heating rate of 12°C min⁻¹

Table 3 Activation energy values

Samples	Activation energy/kJ mol ⁻¹	R ²
CAP 40	84.47	0.99
SBS 440/02	120.29	0.99
L 1861/04	59.23	0.98
L 784/05	95.80	0.99
L 2000/04	80.43	1.00

**Fig. 11** Comparison of FTIR spectra of asphalt samples, CAP 40, SBS 440/02, L 1861/04, L 784/05 and L 2000/04

spectra presented similar absorption bands, a stretching on the C–H bond occurred at frequencies between 2920 and 2851 cm⁻¹. There are also two bands characteristic for aromatic at 1600 and 1456 cm⁻¹. It's relevant to say that these comparison spectra of samples suggest that by the 'fingerprint' bands (866, 808, 740, 722 cm⁻¹) the asphalts were originated from a light oil.

Conclusions

The present study demonstrates thermal analysis combined with FTIR proved to be an effective tool for characterization of the asphalts mixtures. TG/DTG and DTA curves for Brazilian asphalt samples when heated from room temperature to 1000°C, reveals one main decomposition stage on the TG, between 290 to 500°C, with mass loss around 80%, suggesting the decomposition of asphaltenes for all of the samples.

The DTG curves presented a different behavior, so these curves were used for kinetic parameters. The sample with SBS exhibited the highest activation energy value; which corroborated with an increase on thermal stability. The comparison FTIR spectra of asphalt mixtures suggest that by the 'fingerprint' bands these asphalt samples were originated from a light oil.

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References

- 1 Y. Yildirim, *Constr. Build. Mater.*, 21 (2007) 66.
- 2 M. V. Kök and A. G. Iscan, *J. Therm. Anal. Cal.*, 64 (2001) 1311.
- 3 M. V. Kök and O. Karacan, *J. Therm. Anal. Cal.*, 52 (1998) 781.
- 4 *Asphalt Binder Testing*, 1st Ed., Asphalt Institute MA-25, USA 2007.
- 5 *The Shell Bitumen Handbook*, 5th Ed., Cambridge, England 2003.
- 6 M. L. A. Gonçalves, M. A. G. Teixeira, R. C. L. Pereira, R. L. P. Mercury and J. R. Matos, *J. Therm. Anal. Cal.*, 64 (2001) 697.
- 7 X. G. Dong, Q. F. Lei, W. J. Fang and Q. S. Yu, *Thermochim. Acta*, 427 (2005) 149.
- 8 Brazilian Institute of Petrol, 'Informações básicas sobre materiais asfálticos', 6th Ed. (1999).
- 9 M. V. Kök, *Energy Fuels*, 12 (1998) 580.
- 10 C. G. Mothé and A. D. de Azevedo, 'Análise Térmica de Materiais', Editora, SP, ISBN 858791620-3 (2002), p. 300.
- 11 H. E. Kissinger, *Anal. Chem.*, 29 (1957) 1702.
- 12 M. V. Kök and C. Acar, *J. Therm. Anal. Cal.*, 83 (2006) 445.
- 13 M. V. Kök, *J. Therm. Anal. Cal.*, 84 (2006) 361.

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