THERMAL DEGRADATION OF BOTH LATEX AND LATEX CAST FILMS FORMING MEMBRANES
Combined TG/FTIR investigation

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Latex collected from natural rubber trees forming membranes can be used as biomaterials in several fields being the temperature a key parameter. Thermogravimetry (TG) coupled to Fourier transform infrared spectroscopy (FTIR) is a useful technique to investigate the thermal degradation of both latex and cast films (membranes), wich were obtained from *Hevea brasiliensis* (RRIM 600 clone) and used without stabilization. The membranes were prepared by casting the latex onto a glass substrate at 65°C for 6 h. The thermal degradation was followed by FTIR spectra acquisition along the process, allowing the identification of the gaseous components evolved upon the thermal treatment. According to TG measurements, the main processes of thermal degradation of the latex and membranes occur at three temperature intervals for both.

Keywords: latex, natural rubber membranes, TG/FTIR coupling, thermodegradation

Introduction

The paper aims to present a study on the thermal degradation of both latex and latex cast films forming membranes produced without the traditional vulcanization agent (sulphur) envisaging a better comprehension of some physical and chemical properties. Recently, the latex has been extensively applied as biomaterials in the pharmaceutical field as angiogenesis inducer [1]. During the process to make the latex suitable to be applied in the human body as a biomaterial it has to pass through different thermal treatments. However, its biological activity is highly dependent on the temperature [2]. Therefore, an investigation of its thermal degradation is necessary. In this context, combined thermogravimetry–Fourier transform infrared absorption spectroscopy (TG/FTIR) analysis was selected since it involves the characterization not only the sample itself but also of the gases evolved from the samples during the heat treatment (or the heating cycle). To illustrate, they were used in the evaluation of reaction kinetics during the pyrolysis in the pharmaceutical area [3], to check the experimental conditions in the quantitative analytical chemistry experiments [4], in the estimation of volatile substances during the thermal degradation/decomposition of polymeric materials [5], thermal degradation process of natural rubber [6, 7], etc.

Polyisoprene is naturally present in the latex of the *Hevea brasiliensis* tree and is the main constituent to form natural rubber [8] (Fig. 1). Natural rubber is a substance composed of long flexible chains, arbitrarily agglomerated and entangled, with a glass transition temperature (T_g) below room temperature [9–13]. Many polymers, including natural rubber are flexible due to the rotation of the simple C–C bindings allowing several conformational forms [10]. Usually the quality of the Brazilian latex is evaluated by simple standard preparations [14]. The quality of the *Hevea brasiliensis* clones is in general, evaluated by tests related to the characteristics of the natural latex such as dry rubber content, alkalinity, plasticity, ash content, colour, acetone extraction and amount of nitrogen. These tests are in most of the cases indirect representatives of the latex properties and correlation among them is not established. However, efforts have
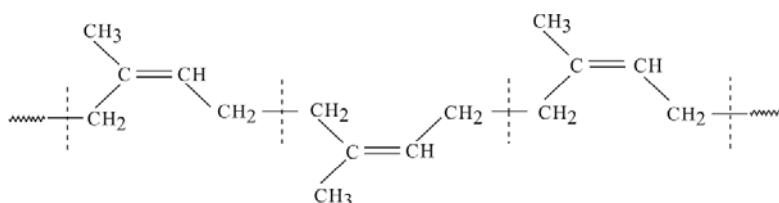

Fig. 1 Molecular structure of the poly *cis*-1,4 isoprene

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been done to improve the quality of the Brazilian rubber considering the effects of the climate and soil on the productivity of the latex and vigour of the rubber trees from several clones, seeking the appropriate fitting of clones to different specific areas in São Paulo State, Brazil [15–20]. For instance, the Agronomic Institute of Campinas (IAC) in Brazil showed that the latex differs from extraction to extraction, affecting the physico-chemical properties of the resulting rubber [21]. Systematic studies concerning latex have been published as well [22–26] combining spectroscopy and microscopy [8] characterizations, morphology and electrical potential studies [27], and colloids and films [28]. Studies of blends containing natural rubber have grown considerably, searching for better properties in different applications [27–30].

Experimental

Extraction of the latex

Latex of rubber tree RRIM 600 clone from Indiana City, in the region of Presidente Prudente, São Paulo State, Brazil, was collected from different trees. All samples were used without stabilization. The characterization of both latex and natural rubber cast films followed by standard procedures described in the Brazilian Association of Standard Methods-ABNT (NBR/11597/1997) [31], which are consistent with those from ISO 2859-1:1989 and ISO/DIS 3951:1989. All reagents were p.a. grade and used as purchased.

Preparation

Natural rubber films with 0.5 mm of thickness forming membranes were prepared by casting the latex as-collected at 65°C for 6 h.

Characterization

The characterization was carried out with a TG/FTIR coupling. Thermal analysis was carried out using the Netzsch equipment (model 204), heating 5.0 mg of each sample in alumina crucible using purified nitrogen gas (15 mL min^{-1}) and at a heating rate of 10°C min^{-1} from 27 to 700°C. FTIR spectra were recorded using a Bruker spectrometer model Vector 22 in the 400–4000 cm^{-1} wavenumber range with 4 cm^{-1} spectral resolution, 32 scans and a DTGS detector.

Results and discussion

Figure 2 shows the TG curves of both latex and membranes. It is observed that the mass loss for both latex

and membranes occurs in three steps mainly. For the latex, the first step occurs 27–80°C with 24% of mass loss. The second step appears between 80–125°C causing 31% of mass loss. Both steps refer to the release of volatile components of the latex. It is important to establish that the average composition of the latex is 1.0–1.8% of proteins, 1.0–2.0% of carbohydrates, 0.4–1.1% of neutral lipids, 0.5–0.6% of polar lipids, 0.4–0.6% of inorganic, 0.4% of amino acids, amines and others, 50–60% of water [32–34]. Therefore, it can be concluded that latex contains about 40% of dry rubber. The third step is observed between 270–420°C with 40% of mass loss, which is attributed to the degradation of poly cis-isoprene molecules. The 5% of residual mass at the end of the thermal degradation process (600°C) is attributed to inorganic ashes as oxides, carbonates, phosphates and metal silicates. For the membranes, the decomposition also happens in three steps, where the first step is between 100–280°C with the mass loss of 10% associated with
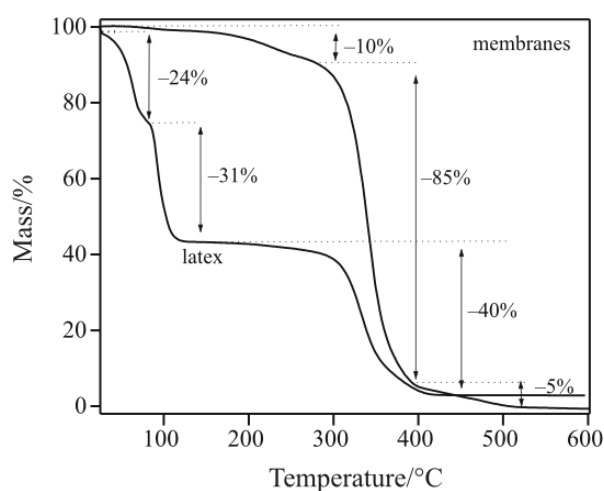
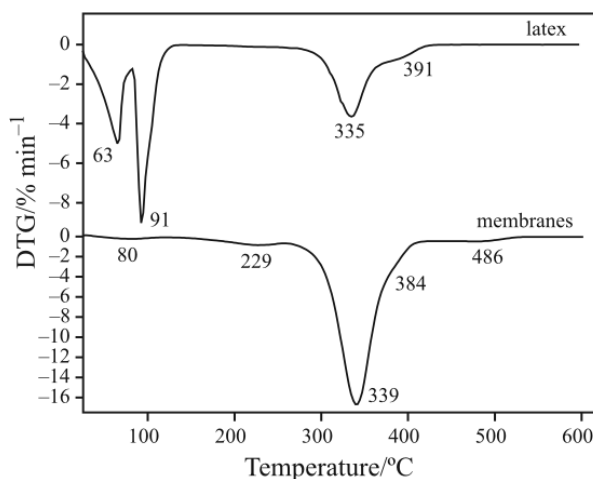**Fig. 2** TG curves of latex and membranes

Fig. 3 DTG curves of latex and membranes

both water evaporation (ca. 1%) and simultaneously chain reticulation and scission. The loss is very small in the case of the reticulation being associated with the formation of aldehydes, ketones and carboxylic acids [32]. The second step occurs between 280–395°C with mass loss of 85% related to the degradation of poly cis-isoprene molecules. The third step between 395–509°C is accompanied by 5% of mass loss is attributed to the degradation of polymeric chains highly reticulated.

Figure 3 presents the DTG curves obtained from the TG curves for the same compounds. The DTG curve shows with more accuracy the irregularities of the baseline revealing the temperatures where the thermal degradation processes takes place with maximum rate. For the latex, the curve has three distinct peaks at 63, 91 and 335°C and a shoulder at 391°C. The DTG peaks are directly related to the TG analysis, where the shoulder is characteristic of degradation of more thermally stable products. For the membranes, the DTG curve shows three unevenness of the baseline at 80, 229 and 486°C, one peak at 339°C with a shoulder at 384°C. The shoulder at 486°C is not present in the TG of the latex. This shoulder is also associated with the degradation of more thermally stable products, which might be related to reticulation or cycling processes.

The TG technique allows the quantitative determination of mass loss process without qualitative indication of the evolved gaseous products. After coupling TG to FTIR the evolved gases have been analysed. The results are summarized in a form of a 3D box where the axes are for the wavenumber, temperature and absorbance values. Figure 4 presents the 3D image of the TG/FTIR measurements of latex. It is observed that the FTIR spectra are concentrated in two different tem-
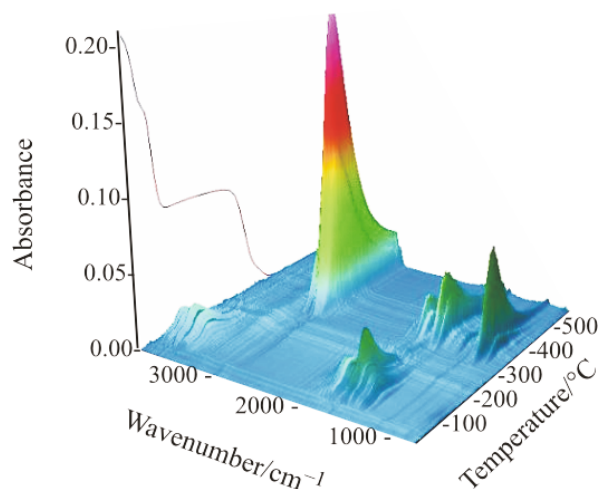
perature ranges. The first range is between 27 and 140°C and the second one from 270 to 420°C. Figure 5 shows three FTIR spectra of the latex extracted from the 3D image presented in Fig. 4, recorded at 93, 338 and 392°C. The assignments of the FTIR absorption bands are listed in Table 1 [35–38].

The bands in the spectra recorded at 93°C are characteristic of the degradation of the latex, where the amides are predominant. Observed bands were: 3960–3490 cm^{-1} from water vapour, 1743 cm^{-1} from C=O ester symmetric stretching, 1710 cm^{-1} from C=O carbonyl symmetric stretching, 1642 cm^{-1} from primary
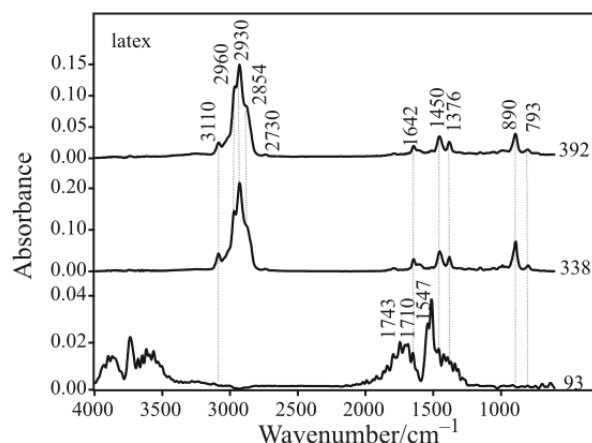
Fig. 5 Latex FTIR spectra at 93, 338 and 392°C extracted from the 3D image shown in Fig. 4

Table 1 FTIR absorption bands of both latex and natural rubber cast film

Latex	Membrane	Attributions
3960–3490	3960–3490	vapour of water
3110	3110	ν_{as} C=C
2960	2960	ν_{as} C–H in the CH$_3$
2930	2930	ν_{as} C–H in the –CH$_2$–
2854	2854	ν_s C–H in the –CH$_2$– [35]
2730	2730	ν CH$_2$ C=CH$_3$ [36]
1743	–	ν_s C=O of ester
1710	1710	ν_s C=O of dimeric acid
1642	1642	primary amide νC=O in connection of H with water
–	1548	secondary amide νCN+NH [37]
1450	1450	δ CH$_2$
1376	1376	δ CH$_3$
890	890	–CH$_3$ wag –C–H of the CH$_2$=C(CH$_3$) [38]
793	–	–CH$_2$– rock [35] –C(CH$_3$)=CH– [36]

ν_{as}=asymmetric, ν_s=symmetric stretching, δ=angular deformation

Fig. 4 3D image containing FTIR spectra as function of temperature for the evaporated gas from latex produced during the TG measurements
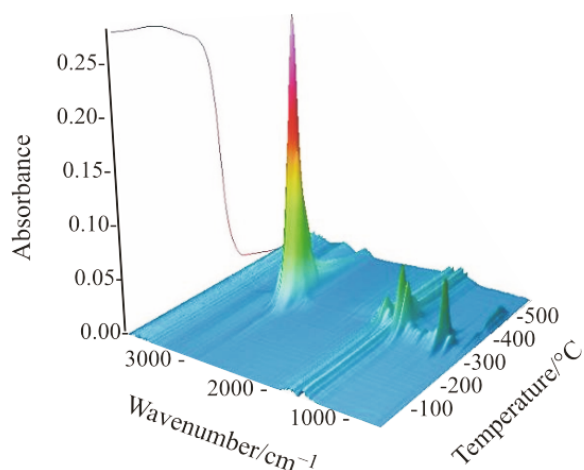
Fig. 6 3D image containing FTIR spectra as function of temperature for the evaporated gas from the membranes produced during the TG measurements
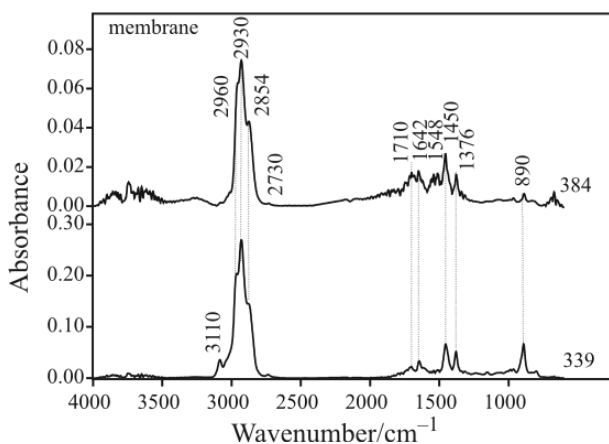

Fig. 7 Membranes FTIR spectra at 339 and 384°C extracted from the 3D image shown in Fig. 6

amide stretching, 1547 cm^{-1} from secondary amide stretching (C–N) and angular deformation (N–H). The FTIR bands in the spectra recorded at 338 and 392°C are related to structural degradation of the dry rubber in the latex, which represents approximately 40% of the latex mass in this case. All the absorption bands at 3110, 2960, 2930, 2854, 2730, 1450, 1376 and 890 cm^{-1} refer to the functional groups present in the natural rubber, being significant the vibration modes attributed to *cis*-1,4 poly-isoprene.

Figure 6 shows the 3D image of TG/FTIR measurements recorded for the membranes. It is observed that differently from latex, the FTIR spectra are concentrated in one temperature range between 270 and 420°C, which refers to the degradation of the dry rubber, as it was previously mentioned. Figure 7 shows two FTIR spectra of the membrane extracted from the 3D image presented in Fig. 6 recorded at 339 and 384°C, which correspond to the structural degradation of the rubber

and are similar to those found in the spectra of the latex recorded at 335 and 391°C (Fig. 4) as expected.

Finally, it must be mentioned that the idea would be to propose a degradation process for the latex caused by heating. In this context we would have two extremes: *i*) the water will simply evaporate and the *cis*-1,4 poly-isoprene will be cleaved in the main chain through C–C bonds; *ii*) on the other hand, the components such proteins, carbohydrates, etc. are complex molecules, whose thermal degradation process requires a comprehensive investigation, which is out of the scope of this paper. According to the surveyed literature the thermal degradation mechanism for latex is a completely opened topic. Besides it must be considered that the amount of components such proteins, carbohydrates, etc. is quite low (up to 4%).

Conclusions

Thermal behaviour of latex and natural rubber cast films forming membranes was characterized by TG/FTIR coupling. The temperature interval of the degradation was determined which is important in the aspect of application of latex as biomaterial. The degradation of latex takes place in three main mass loss steps. The first two are between 27 and 125°C leading to ca. 55% of mass loss caused by the decomposition of proteins, amino acids, carbohydrate, lipids and nucleic acids. The third step starts at 270°C and corresponds to the degradation of the 40% of dry rubber leading to the degradation of the polyisoprene molecules. In the case of membranes, the mass loss occurs in three steps as well where the step two between 280 and 395°C is the most significant one with a mass loss of 85% being assigned also to the thermal degradation of the dried rubber.

Acknowledgements

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