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Determination of intrinsic viscosity of poly(ethylene terephthalate) using infrared spectroscopy and multivariate calibration method

M.A. Silva Spinacé [a], M.U. Lucato [a], M.F. Ferrão [b], C.U. Davanzo [a], M.-A. De Paoli [a,*]

[a] *Instituto de Química, Universidade Estadual de Campinas, C.P. 6154, 13084-971, Campinas-SP, Brasil*

[b] *Departamento de Química e Física, Universidade de Santa Cruz do Sul, C.P. 188, 96815-900, Santa Cruz do Sul-RS, Brasil*

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Abstract

A methodology was developed to determine the intrinsic viscosity of poly(ethylene terephthalate) (PET) using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and multivariate calibration (MVC) methods. Multivariate partial least squares calibration was applied to the spectra using mean centering and cross validation. The results were correlated to the intrinsic viscosities determined by the standard chemical method (ASTM D 4603-01) and a very good correlation for values in the range from 0.346 to 0.780 dL g^{-1} (relative viscosity values ca. 1.185–1.449) was observed. The spectrophotometer detector sensitivity and the humidity of the samples did not influence the results. The methodology developed is interesting because it does not produce hazardous wastes, avoids the use of time-consuming chemical methods and can rapidly predict the intrinsic viscosity of PET samples over a large range of values, which includes those of recycled materials.

Keywords: Diffuse reflectance; Intrinsic viscosity; Poly(ethylene terephtalate); Multivariate calibration; PET

1. Introduction

Intrinsic viscosity measurements are routine quality control procedures required by industries working with virgin or recycled poly(ethylene terephthalate) (PET). This occurs because intrinsic viscosity is related to the average molar mass, and this variable influences the processing and the final mechanical properties of the polymer. Correlations of intrinsic viscosity to other properties are observed if the polymer chain is linear and the molar mass presents low dispersions, as in the case of PET [1]. PET intrinsic viscosity determinations made according to ASTM D 4603-01 [2] need toxic and expensive solvents (phenol and tetrachloroethane) and are time-consuming. The results are subject to operational errors and produce a large amount of hazardous waste.

Presently, the use of multivariate calibration (MVC) methods is increasing in situations where it is difficult to measure the parameter of interest in a direct way [3]. MVC methods are used in a wide variety of industrial applications, e.g. in the food, petroleum or pharmaceutical industries. Generally, MVC methods are associated to spectroscopic techniques like reflection spectrophotometric techniques in the mid-infrared, because this technique presents low cost, simplicity and short measurement times. Moreover, it generates spectra with good signal-to-noise ratios that can be obtained using solid powdered samples [4–11]. However, special care is necessary using correlations from reflectance spectra in the mid-infrared, because these spectra can be severely distorted by specular reflections and by differences in the optical path of the diffusely reflected light [12–14]. The use of MVC methods to estimate several polymer properties, aiming to characterization of polymeric materials, has been described in the literature [15–17]. The main purpose of MVC methods is to establish a relationship between two data matrices, one containing chemical or physical information and another containing the spectral signal for many wave numbers. Partial least squares (PLS) regression is the most widely used MVC method for laboratory and industrial purposes and has been employed in a large variety of applications in chemical analysis [18–27].

The literature reports the use of MVC methods associated with near infrared transmission spectroscopy (NIRS) to determine the relative viscosity of PET in the range from 1.50 to

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[*] Corresponding author. Tel.: +55 19 3788 3075; fax: +55 19 3788 3023.
E-mail address: mdepaoli@iqm.unicamp.br (M.-A. De Paoli).

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1.60 [28]. In this work, MVC method combined with diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was used to develop a quantitative analytical methodology, without generating chemical residues, to determine relative viscosity of PET over the range from 1.185 to 1.449. We choose to study this range of relative viscosity, because it includes the values for recycled materials. The use of FTIR–DRIFTS, in comparison to near-infrared spectroscopy, was preferred because this technique requires only an accessory and a conventional FTIR spectrophotometer and it can be also used to identify functional groups in the polymer. As references, intrinsic viscosities were measured according to ASTM D 4603-01. The influence of distorted regions in the DRIFTS spectra and the humidity of the samples were also studied.

2. Experimental

2.1. Preparation of the samples for building the calibration matrix

Virgin PET pellets (RHOPET® S80, intrinsic viscosity = 0.80 dL g^{-1}) were supplied by Rhodia-Ster S.A (Poços de Caldas, Brazil). The samples were dried at 160 °C for 6 h prior to processing and were reprocessed by extrusion using a Wortex model WEX30 (Campinas, Brazil) single-screw extruder ($L/D = 30$, $D = 32$ mm). The thermal profile used was 220–280 °C from the feeding zone to the die, and the rotational speed was 102 rpm. A group of 20 samples plus virgin PET were obtained.

2.2. Determination of intrinsic viscosity of the PET samples

All samples were ground in a knife-mill (Thomas-Wiley Mill, ED-5) and dried under vacuum at 160 °C for 4 h (Tecnal model EDGCON 5P) prior to intrinsic viscosity measurements. Intrinsic viscosity was measured in triplicate at 30 °C using a 60/40 (w/w) phenol/1,1,2,2-tetrachloroethane solvent mixture, according to ASTM D 4603-01, in a Cannon-Ubbelohde viscosimeter.

2.3. Spectroscopic measurements

The transmittance spectrum of PET film (0.11 mm thickness) was measured from 4000 to 500 cm^{-1} in a Bomem MB-100 spectrophotometer with a deuterated triglycine sulfate (DTGS) detector and a resolution of 4 cm^{-1}. The attenuated total reflectance (ATR) spectrum of PET film was obtained in a Nicolet 520 spectrophotometer with a DTGS detector using a horizontal ATR accessory and a ZnSe crystal. These spectra were measured from 4000 to 650 cm^{-1}, with a resolution of 4 cm^{-1}.

The DRIFTS spectra of PET powder (65 mesh) were obtained in a Bomem DA-8 spectrophotometer using a HgCdTe (MCT) detector cooled by liquid N_2 or in a Bomem MB-100 equipped with a DTGS detector. DRIFTS spectra were measured from 4000 to 500 cm^{-1} with a resolution of 4 cm^{-1} by co-adding 256 spectra that were processed with apodization of two types: Happ-Genzel for DA-8 and cosine for the MB-100. The spectra were obtained from the powder without dilution. The resulting spectra were normalized by dividing with a reference spectrum obtained with the empty sample support of the DRIFTS accessory and these ratios R were used as $\log(1/R)$. The DRIFTS spectra were obtained for dried and undried PET samples. For the dried samples, the PET powders were dried under vacuum at 160 °C for 6 h and handled in a glove box with dry N_2. The sample support of the DRIFTS accessory was filled with the powder, quickly transferred to the sample compartment of the Bomem DA-8 equipment and the spectra were measured under vacuum. For undried samples, PET powders were maintained in a saturated water atmosphere overnight and the spectra were obtained at ambient atmosphere with the Bomem DA-8 and MB-100 instruments.

2.4. Calibration and validation methods with preprocessing

The calibration and validation steps were carried out with multivariate methods including partial least squares regression (PLS). Prior to calibration modeling, data preprocessing were applied using scaling and signal correction. All regression analyses were made using the software Unscrambler 6.11.

3. Results and discussion

To establish a quantitative model, the intrinsic viscosity values of 21 samples, prepared as described in Section 2.1, were determined according to ASTM D 4603-01 (Table 1). These samples presented values in the range from 0.346 to 0.780 dL g^{-1} (relative viscosity values ca. 1.185–1.449), which are typical for post-consumer PET. A similar analysis has been reported [28] but using NIRS and PET samples with relative viscosity values from 1.50 to 1.60.

3.1. Spectra preprocessing

To construct the calibration model, we initially did preprocessing, because the surface scattering and the specular reflection cause baseline variations and wavelength shifts in measured spectra of powder samples resulting in spectra with considerable

Table 1
Values of the PET intrinsic viscosity used in the calibration set

Sample	Intrinsic viscosity (dL g^{-1})	Sample	Intrinsic viscosity (dL g^{-1})
1	0.3458	11	0.5389
2	0.3656	12	0.5558
3	0.3682	13	0.5574
4	0.4076	14	0.5769
5	0.4210	15	0.6051
6	0.4479	16	0.6443
7	0.4780	17	0.6476
8	0.4853	18	0.6578
9	0.4927	19	0.6910
10	0.5129	20	0.7009
		21	0.7800

noise [29]. To reduce these effects two types of preprocessing are often used, differentiation and signal correction. Thus, all DRIFTS spectra data were preprocessed using the first derivative, normalization through the strongest peak and mean centering [30] followed by multiplicative signal correction [31,32] to improve the performance of the method.

3.2. Calibration and validation methods

Several algorithms can be used to develop predictive models. In this paper we used the PLS, that is a method based on factorial analysis that has been much used for MVC methods. In this method, an ***X*** matrix is constructed with m columns containing the spectral signals (e.g. absorbance) at each wavenumber and n rows representing samples. A second matrix, ***Y***, is constructed with k columns with chemical or physical information (e.g. concentration, viscosity, etc.) and n rows corresponding to samples. The PLS tool is applied to decompose ***X*** and ***Y*** into smaller matrices, called the latent variable (LV). A correlation can be written with these latent variables using the components of the smaller matrices. PLS [18] was used to correlate spectral information with PET intrinsic viscosity. The best number of LV was determined by the minimum value of a predictive residual sum of squares (PRESS, Eq. (1)), defined as the sum of the squared deviations for the unknown values, estimated in relation to the real values, where y_i is the reference value for the ith sample, $\hat{y}_i$ the predictive value of this sample, and n the number of the calibration samples.

$$\text{PRESS} = \sum_{i=1}^{n}(y_i - \hat{y}_i)^2 \quad (1)$$

The model was validated by the "leave-one-out" method using the calibration set and a root mean square of prediction (RMSEP, Eq. (2)) was calculated. A cautious analysis of this value can also help in selecting the number of LV.

$$\text{RMSEP} = \frac{1}{n-1}\sqrt{\sum_{i=1}^{n}(y_i - \hat{y}_i)^2} \quad (2)$$

The relative mean error (RME) also was considered, Eq. (3).

$$\text{RME}\,(\%) = \frac{\sum_{i=1}^{n}|y_i - \hat{y}_i|/y_i}{n} \times 100 \quad (3)$$

The smallest RMSEP or LV values were used as criteria to choose the best preprocessing method of the DRIFTS spectra. It was observed that only mean centering showed the smallest RMSEP or LV values, so it was then used in subsequent trials. After that, the models were constructed starting with three different ***X*** matrices; the first one with the DRIFTS spectra data of undried PET powders using the DTGS detector and the other two related to dry and undried PET powders obtained by DRIFTS using the MCT detector. The ***Y*** matrices were reference values for intrinsic viscosity obtained according to ASTM D 4603-01. Preliminary studies were performed with the PLS method using the range from 4000 to 600 cm^{-1} with both matrices using mean centered values. The regression analyses were carried out through the cross validation method due the small number of samples [22]. In this validation method, one sample was subtracted from the group of n samples and $\boldsymbol{n} - 1$ samples were used to construct the calibration group. Following this, the calibration group is used to predict the value of the remaining (excluded) sample. This procedure was repeated for all samples, resulting in predictions for all samples by the "leave one out" method. Therefore, it was possible to calculate the PRESS values considering the prediction errors for all samples. The LV was selected to produce a minimum PRESS value. Correlation coefficient (R^2), RMSEP and RME values were calculated for this LV (Table 2).

3.3. Influence of distorted spectral regions and humidity of the samples in the models

PET samples with particle sizes of 65 mesh are too large for a diffuse reflectance measurement, resulting in distorted spectra and influencing the MVC models [12–14]. To reduce this effect, the DRIFTS spectra of PET powders were analyzed to identify and exclude distorted regions to construct the MVC models.

Table 2
Calculated linear regression (R^2), LV number (LV), root mean square error of prediction (RMSEP), relative mean error (RME) and spectral regions used in each model

Description Of samples	Detector	R^2	LV	RMSEP	RME (%)	Regions (cm^{-1})
Dried	MCT	0.9687	4	0.033	5.095	All[a]
Dried	MCT	0.9595	3	0.037	5.172	2660–3650[b]
Dried	MCT	0.9580	3	0.038	5.054	2660–2850, 3010–3650[c]
Undried	MCT	0.9725	4	0.032	4.840	All[a]
Undried	MCT	0.9565	3	0.038	5.517	2660–3650[b]
Undried	MCT	0.9592	3	0.037	4.859	2660–2850, 3010–3650[c]
Undried	DTGS	0.9600	4	0.037	5.714	All[a]
Undried	DTGS	0.9660	3	0.034	4.975	2660–3650[b]
Undried	DTGS	0.9674	3	0.034	5.178	2660–2850, 3010–3650[c]

[a] Refers to Fig. 2(a).
[b] Refers to Fig. 2(b).
[c] Refers to Fig. 2(c).

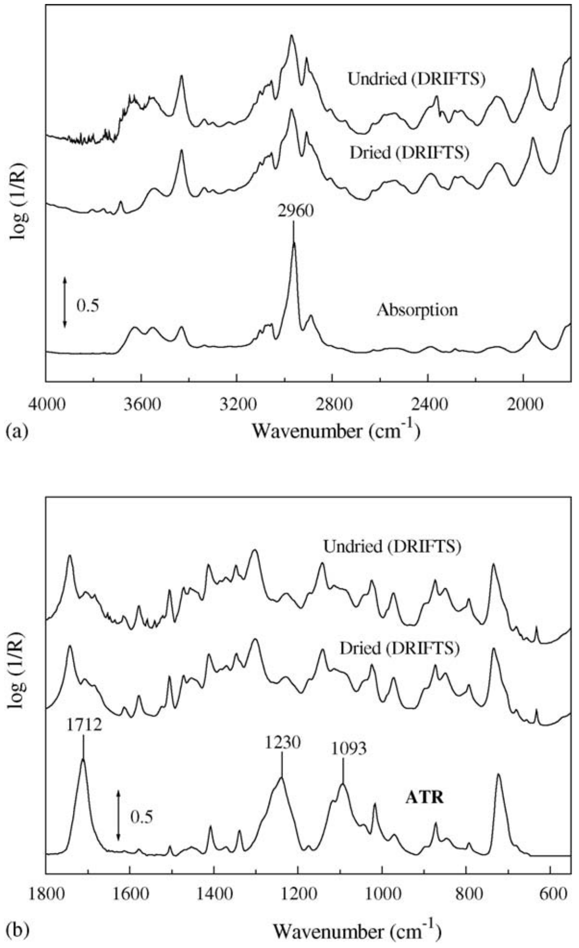

Fig. 1. FTIR spectra of the first extrusion cycle for: (a) DRIFTS spectrum of undried and dried PET powder samples; absorbance spectrum of PET film in the range from 4000 to 1800 cm^{-1}; (b) DRIFTS spectrum of undried and dried PET powder samples and ATR spectrum from 1800 to 500 cm^{-1}.

Initially, the spectra of PET powders, measured by DRIFTS, were compared to PET film spectra obtained by transmittance and by the attenuated total reflectance (ATR) technique (Fig. 1). The DRIFTS spectra of PET powders were compared to the transmittance spectra of PET film and appropriately scaled spectra were observed in the range from 4000 to 1800 cm^{-1}. In the range from 1800 to 600 cm^{-1} it is not possible to obtain appropriately scaled spectra by transmittance from film due to very strong bands. Thus, for this range, the DRIFTS spectra of PET powders were compared with spectra of PET film obtained by the ATR technique and with intensities corrected for wavelength dependence.

The spectra of PET films obtained by transmittance and the DRIFTS spectra of dry and undried PET powders are shown in Fig. 1(a). The spectra of PET film obtained by transmittance showed the strongest band at 2960 cm^{-1}. In the DRIFTS spectra of dry and undried samples, this band was slightly shifted to 2970 cm^{-1}, and the values of relative intensity of other bands were different from the values obtained using transmittance. These distortions are probably due to specular reflection components. All other bands occurring in the range from 4000 to 800 cm^{-1} have similar intensities in both transmittance and reflectance. It is worth noting that the DRIFTS spectra of the undried PET samples showed a peak due to moisture content near the absorption at 3630 cm^{-1} (Fig. 1(a)).

In the spectra of PET film obtained by ATR (Fig. 1(b)), after intensity correction for wavelength dependence, three strong bands at 1712, 1230 and 1093 cm^{-1} could be observed. These are characteristic of the ester moiety of the PET polymer. The DRIFTS spectra of dried and undried PET samples were very similar. However, distortion due to specular reflection occurs and these bands are shifted to 1750, 1300 and 1150 cm^{-1}, respectively.

The spectral regions relevant to the construction of the predictive models are shown in Fig. 2. For the construction of the calibration models, three spectral regions of the spectra of dried and undried PET samples using the MCT and DTGS detectors were used, resulting in nine calibration models (Table 2). The regression coefficients as a function of spectral range of non dried PET samples for the range from 4000 to 500 cm^{-1}, *first spectral region*, showed similar profiles for data acquired using MCT and DTGS detectors (Fig. 2(a)). The range from 1700 to 1400 cm^{-1} was quite variable for undried samples, due to noise related to the strong bands of water absorption, but almost not influenced for the dried samples. Based on this result, and due to the fact that below 1800 cm^{-1} the spectra were quite distorted, as previously discussed (Fig. 1), this region was excluded from the calibration models. The spectral range from 2660 to 1800 cm^{-1} was also excluded, because it did not provide relevant information. Consequently, multivariate regression was calculated using the range from 3650 to 2660 cm^{-1}, *second spectral region* (Fig. 2(b)). In this case, the LV decreased and there were no significant improvements in RMSEP and RME. Finally, the range from 3010 to 2850 cm^{-1} was also excluded from the overall range from 3650 to 2660 cm^{-1}, resulting in the range from 2660 to 2850 cm^{-1} and from 3010 to 3650 cm^{-1}, *third spectral region*. This exclusion was made to verify the influence of the distorted intensity of the band near 2970 cm^{-1} (Fig. 2(c)).

The LV value was chosen for all models when the PRESS value was *minimum*, as illustrated for different models in Fig. 3. The models obtained using the first spectral region presented LV equal to 4 and this value decreased to 3 when the second and third spectral regions were used. This LV value of the models that used the first spectral region can be related to the distorted regions, which were excluded in the models that used the second and third spectral regions. However, this decrease of LV from 4 to 3 is insignificant for the MVC models, since RMSEP and RME values did not change. Besides, the use of different detectors and PET powders with or without drying produced similar values of R^2, LV, RMSEP and RME (%), indicating that these factors did not influence the results of the MVC models (Table 2). The calibration and predictive (validation) values were practically coincident (Fig. 4) indicating good predictive capacity of these models. The standard deviation of the reference method (ASTM D 4603-01) is ca. 1% and the RME (%) obtained in the calibration models was ca. 4–5%.

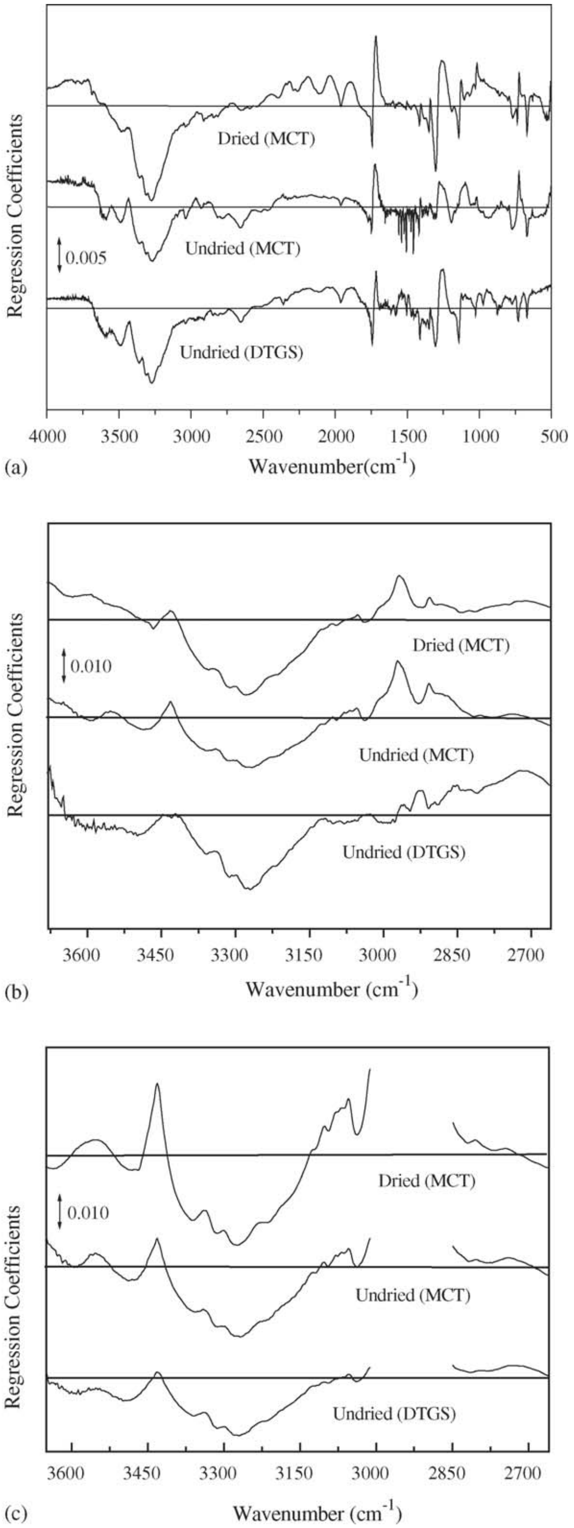

Fig. 2. Regression coefficients as a function of spectral range: (a) from 4000 to 500 cm^{-1}; (b) from 3650 to 2660 cm^{-1} and (c) from 3650 to 3010 and from 2850 to 2660 cm^{-1}.

3.4. Other figures of merit

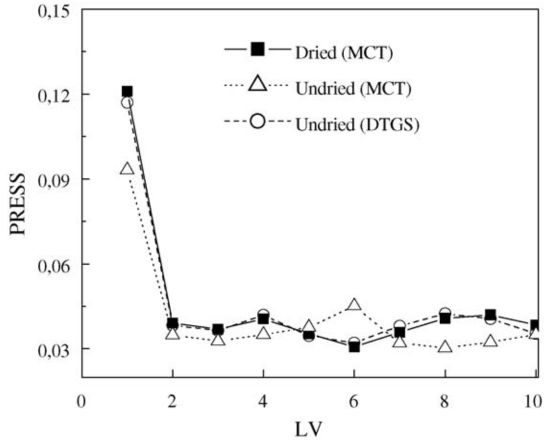

Fig. 3. Predictive residual sum of squares (PRESS) against LV number (model using subregions from 3650 to 3010 and 2850 to 2660 cm^{-1}).

The concept of net analyte signal (NAS) [33–36] was employed to determine the sensitivity (SEN) and the selectivity (SEL). The equations were performed in MATLAB using the modification proposed by Ferré et al. for inverse multivariate models [37]. In this approach, NAS is calculated for the spectrum projected onto the regression latent variables. The sensitivity (SEN) is defined as amount of signal that, in prediction, corresponds to a concentration equal to unity [33,35] and can be seen as the slope of the calibration line. The selectivity (SEL) is the fraction of the signal that is unique to the analyte and can be defined as the ratio between the net and the gross signal [38,39]. The selectivity quantifies the loss of signal due to other analytes or due to interferents and ranges from zero (no selectivity) to one (full selectivity).

The result of the sensitivity (SEN) and the selectivity (SEL) for the models using the first spectral region (4000–500 cm^{-1}) for dried and undried samples, with two different detectors, are shown in Table 3. The sensitivity obtained for these tree models, with different experimental conditions, was similar, indicating that both detectors are appropriate to determine the intrinsic viscosity of PET samples. Besides, it is not necessary to dry the samples. The values of the selectivity obtained for all the calibration models are relatively large indicating that these do not represent a significant loss of signal.

3.5. Attribution of the main bands related to the MVC models

After the construction of the MVC models, the main bands related to the calibration process were attributed. This is not an easy task due to the presence of fundamental transitions, bands of overtones and combinations, overlaps and other bands related to the carbon chain of PET. In the range from 3700 to 3500 cm^{-1} the absorptions related to the O–H stretching frequency of hydroxyl end groups appear at 3547 cm^{-1} [40]. For undried PET samples, the bands related to this mode of vibration show partial overlap with water absorption and were very broad, starting at 3756 and 3657 cm^{-1} (anti-symmetric and symmetric –OH stretching). The peak at 3431 cm^{-1} is related to the second carbonyl overtone (C=O), whose fundamental transition occurs at ca. 1715 cm^{-1}.

Table 3
Figures of merit for tree PLS models constructed with full spectral region

Description of samples	Detector	LV	Regions (cm^{-1})	SEN ($\log(1/R)$, $dL\,g^{-1}$)	SEL (average)
Dried	MCT	4	500–4000	3.69×10^{-4}	0.757
Undried	MCT	4	500–4000	3.90×10^{-4}	0.803
Undried	DTGS	4	500–4000	4.23×10^{-4}	0.799

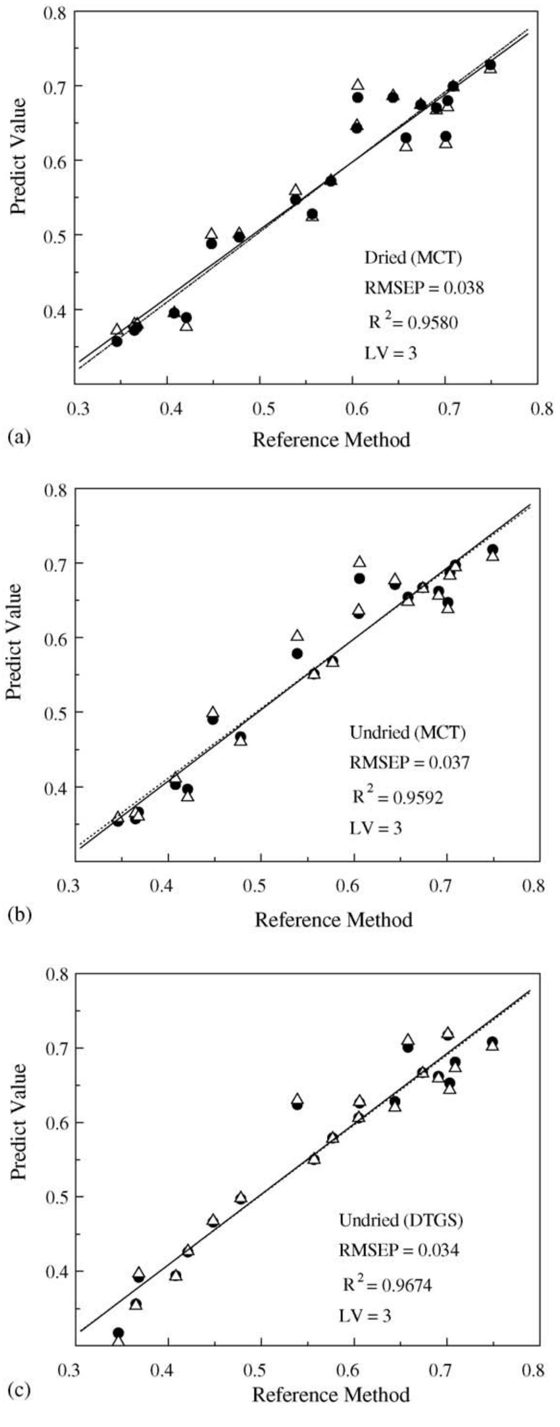

Fig. 4. Plots of reference method against predicted values: (a) dried samples (MCT); (b) undried samples (MCT) and (c) undried samples (DTGS). The symbol (▲) is the prediction sample and (●) the calibration sample.

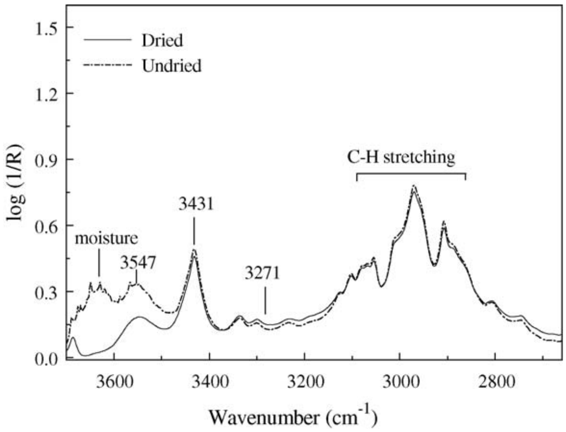

Fig. 5. DRIFTS spectra of dried and undried PET powder samples, range from 3695 to 2662 cm^{-1}.

The range from 3229 to 3335 cm^{-1} is the region where important bands for model construction are found and include the peak at 3271 cm^{-1}, related to the carboxyl end group, which overlaps with other absorptions of the carbon chain [40]. The regression plot in Fig. 2 showed that the maximum value of the regression coefficient corresponds to absorption at 3271 cm^{-1}, indicating the relevance of this region (3229–3335 cm^{-1}) for the models.

The bands related to hydroxyl and carboxyl end groups of PET are very important for the models because they are correlated with molar mass and, consequently, to the intrinsic viscosity of PET [40–43]. When degradation of PET occurs, its intrinsic viscosity decreases and the number of hydroxyl and carboxyl end groups increase. Thus, there is an inverse relation between these properties and the intensity in the regions related to carboxyl and hydroxyl end groups, which can be used in the prediction of intrinsic viscosity.

Although the bands related to hydroxyl and carboxyl end groups of PET are very important to the models, the range from 3100 to 2660 cm^{-1} (Fig. 5) has bands related to C–H stretching that were also used in the modeling. If this region is excluded from the model, RME increases, indicating its importance.

4. Conclusions

The methodology developed demonstrated that it is possible to determine the intrinsic viscosity of recycled PET with good correlation using DRIFTS associated with MVC methods. PLS with mean centered values was used and the regression analyses were carried out through the cross validation method. The distortion of the spectra did not influence the construction of the models and their predictive capability. The results indicate that it is possible to construct models to determine the intrinsic viscosity of undried PET samples using an infrared spectrophotometer with a conventional detector.

This methodology has some advantages, such as simple sample preparation, easy operation and short analysis time, in addition to the absence of chemical residues.

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