

## Prediction of Mechanical Properties of Poly(ethylene terephthalate) Using Infrared Spectroscopy and Multivariate Calibration

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**ABSTRACT:** This work describes a method to determine mechanical properties (tensile strength at break and tensile modulus) of poly(ethylene terephthalate) using median infrared spectroscopy and multivariate calibration. Infrared spectroscopy is very promising for polymer process control and final product analysis because it is rapid and nondestructive. The spectra of the films were obtained using two techniques: attenuated total reflection and direct transmission. The spectra were subjected to various preprocessing procedures, such as smoothing and derivative using the algorithm Savitzky-Golay, standard normal variate, multiplicative scatter correction and, as well, combinations of some of these preprocessing techniques. The predictive ability of the regression models were evaluated using an external validation set. The regression techniques used, partial least square and multiple linear regression, showed, in general, comparable results with root mean square error of prediction similar to the repeatability of the conventional method used to determine these mechanical properties (1.3 kgf/mm<sup>2</sup> for tensile strength at break and 29.6 kgf/mm<sup>2</sup> for tensile modulus).

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### INTRODUCTION

Poly(ethylene terephthalate) (PET) is a well-known engineering plastic that offers excellent performance in a variety of applications such as in the film, fiber, and packaging industries.<sup>1–3</sup> Its use in these different industries is mainly due to its properties such as its gas barrier, excellent chemical resistance, mechanical and thermal properties, good optics, and relatively low cost of its raw material.<sup>4,5</sup>

The growth of the world production of PET<sup>4</sup> has increased the need to develop methodologies for rapid and effective quality control of the polymer. Among the quality parameters of polymers, the mechanical property is the most important and arouses the most technological interest. Tensile strength at break, tensile modulus, and percentage elongation properties are mechanisms that serve as comparison parameters to measure the mechanical performance of the different polymers.<sup>6</sup> The determination of the mechanical properties of these polymers is important to ensure the quality and specifications required for the numerous applications. Currently, these properties are determined by mechanical tests using a universal testing machine.

Although mechanical testing is effective, it is not efficient in that it is destructive and time-consuming. Therefore, simple, fast, effective, relative low cost, and nondestructive methods, which can be used with the same effectiveness as the reference method, have become very attractive. In this context, infrared spectroscopy combined with multivariate calibration is a technique that has been successfully applied to various areas such as agriculture,<sup>7–9</sup> food,<sup>10–12</sup> pharmaceutical,<sup>13–15</sup> fuel,<sup>16–18</sup> and paper.<sup>19,20</sup>

Given the diversity of applications, near and median infrared spectrometric (NIR and MIR) techniques are very promising means of determining polymer properties. Infrared spectroscopy, when used as an analytical quantitative tool, might be called a secondary technique; that is, it is necessary to build a multivariate model to correlate the infrared spectra (matrix **X**) with the corresponding values of the property of interest (vector **y**), previously determined by a reference method. After validation of the method, the properties can be monitored and evaluated using infrared spectra. The main advantage of these techniques is to decrease the time and cost of the analysis conducted in the laboratory, because speed combined with

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efficiency in the determination of quality parameters of the material is essential for the control of industrial processes. In addition, samples are not destroyed during the analysis, which provides quality control for the whole batch instead of only for a few samples.

Works have been reported using NIR and MIR spectroscopy combined with chemometric techniques to evaluate properties of polymers. Zhu and Hieftje<sup>21</sup> determined the intrinsic viscosity and concentration of poly(butylene terephthalate)-PBT blends of polycarbonate using NIR spectroscopy and multiple linear regression (MLR). The correlation coefficients of the predicted (using NIR/MLR) versus reference values were 0.979 (for intrinsic viscosity) and 0.955 (for concentration), respectively. Shimoyama et al.<sup>22</sup> determined the density of linear low density polyethylene pellets using NIR spectroscopy and partial least squares regression (PLS). The PLS model showed satisfactory results with a correlation coefficient of 0.970. Ozzetti et al.<sup>23</sup> determined the tacticity of blends of polypropylene with MIR spectroscopy using PLS and principal component regression. The errors incurred for both models were up to five times lower than the errors found using the reference method (<sup>13</sup>C-NMR). Camacho et al.<sup>24</sup> determined the moisture content of recycled nylon using NIR spectroscopy and PLS models. This method was efficient, with a RMSEP (root mean square error of prediction) of 0.05% (w/w). Spinacé et al.<sup>25</sup> determined the intrinsic viscosity of PET using MIR spectroscopy and PLS models. The results showed a high correlation (0.9580, 0.9592, and 0.9674) for values ranging from 0.346 to 0.780 dL g<sup>-1</sup>. Blanco et al.<sup>26</sup> determined the acid value and hydroxyl value in samples taken during the manufacture of polyester resins, using NIR spectroscopy and PLS models. The models showed satisfactory predictive capability for the three properties. Patel et al.<sup>27</sup> determined polyvinyl alcohol percentage (PVOH) in vinyl acetate-alcohol resins (VAAR) using NIR spectroscopy and PLS models. An excellent correlation coefficient (0.9997) was obtained in determining this property, showing that the technique can be applied successfully and precisely to determine the percentage of PVOH in VAAR samples in a methyl acetate: methanol solution with the following compositions (in volume): 80 : 20; 78 : 22, and 82 : 18.

In this work, methods were developed based on MIR and chemometrics to determine the mechanical properties of PET. Models were built using spectra data obtained by direct transmission and using the attenuated total reflection (ATR) technique. The results obtained with two multivariate calibration methods (partial least squares—PLS and multiple linear regression—MLR), using different preprocessing techniques, were evaluated and compared.

## EXPERIMENTAL

### Samples

Ninety-five samples of PET films, 12 μm thick, were collected from different batches obtained from an industry located in Pernambuco State, Brazil (Pernambuco).

### Exposition to Gamma Radiation

To increase the range of the mechanical property variations of the industrial samples, without losing the main polymer features, 48 films were exposed to gamma radiation, using radiation from a cobalt-60 (<sup>60</sup>Co) source with different doses (25, 60, 120, 240, and 500 kGy), using Gammacell, model GC 220 equipment.

### Record of the MIR Spectra

The spectra of all samples of PET films were obtained both by direct transmission and ATR using a spectrophotometer ABB-Bomem, model FTLH 2000-154. The spectra were recorded at room temperature 23°C ± 1°C in the spectral range from 600 to 4000 cm<sup>-1</sup>, with resolution 4 cm<sup>-1</sup> and eight scans. The median time to record the spectrum of each polymer sample was ~ 23 s.

### Reference Method

The reference method used was mechanical tests in a universal testing machine (Instron 4301, model 2365). The mechanical tests were performed according to ASTM D 882 (Method for Tensile Properties of Thin Plastic Sheeting). The tests were carried out using films with the dimensions of (200.0 × 15.2) ± 1.0 mm<sup>2</sup> and the distance between the grips was 100.0 mm at room temperature. The mechanical properties studied in this work were the tensile strength at break and tensile modulus.

### Calibration Models

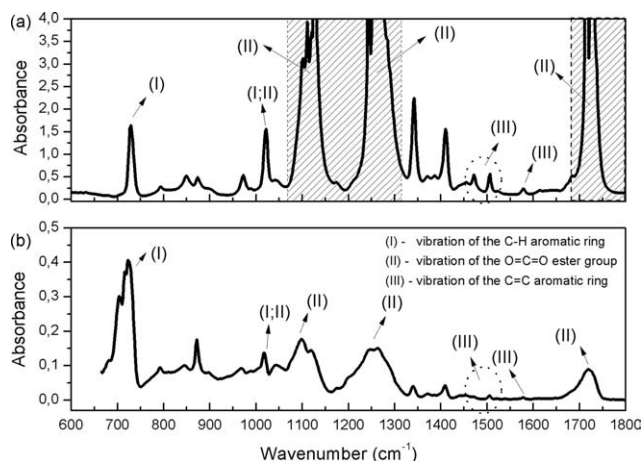
Multivariate models were developed using PLS and MLR. Several preprocessing were evaluated such as: smoothing and first derivative using the Savitzky-Golay algorithm, with windows of 5, 7, 9, 11, 13, 15, and 17 points and second-order polynomial; standard normal variate (SNV) and multiplicative signal correction (MSC), as well as combinations of these. The anomalous samples were detected and excluded from the calibration sets after evaluating their leverage, spectral (X) residue, and the property of interest (y) residue. The selection of samples for calibration (62) and prediction (30) sets were made using the SPXY (Sample set partitioning based on joint x-y distances) algorithm.<sup>28</sup> All models were obtained using full cross-validation to determine the number of factors (PLS) or number of variables (MLR). PLS models were built using only the variables which corresponded to the significant regression coefficients chosen by using the Jack-Knife.<sup>29</sup> Variables selection for MLR models was carried out by using the successive projection algorithm (SPA). The essence of SPA consists of projection operations carried out on a calibration matrix. The SPA builds an ordered chain of variables where each element is selected to present the lowest colinearity (highest orthogonality) with respect to the previous ones. The best performing chain is selected to contain the most valuable variables to be included in a MLR model.<sup>30</sup>

The predictive ability of MLR and PLS models was evaluated based on an external validation set. The data treatment was performed using UnscramblerX<sup>®</sup> and Matlab R2010a<sup>®</sup> software.

## RESULTS AND DISCUSSION

### MIR Spectra

The spectral region selected to build the calibration models was from 650 to 1800 cm<sup>-1</sup>, given the presence of informative PET

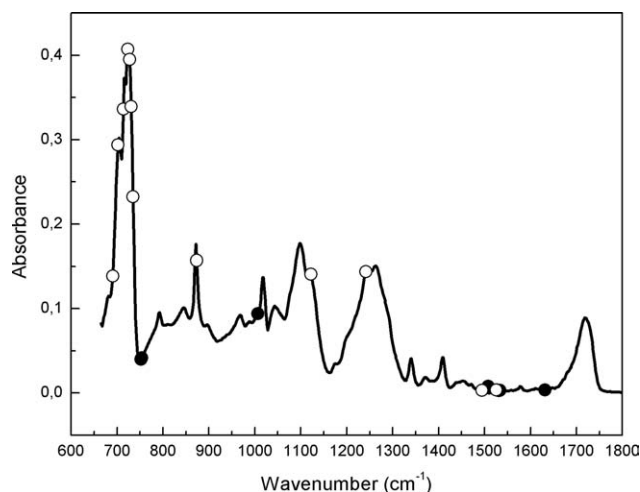


**Figure 1.** MIR spectrum obtained by (a) direct transmission and (b) ATR mode.

bands and satisfactory signal/noise ratio. The MIR spectra of the polymeric samples were obtained using direct transmittance and ATR, as shown in the Figure 1(a) and (b), respectively. The main characteristic absorption bands of PET films can be observed in its IR spectrum (Figure 1), such as: OCO ester vibrations (1720, 1264, 1245, 1098, and 1016  $\text{cm}^{-1}$ ), CH aromatic vibrations (1016 and 724  $\text{cm}^{-1}$ ), and vibrations of the C=C aromatic bonds (1471, 1507, and 1580  $\text{cm}^{-1}$ ). As can be

**Table I.** Initial (Industrial Range), Extended Parameter Range, and Repeatability of the Mechanical Properties of PET Films

Property	Industrial range (kgf/mm <sup>2</sup> )	Extended parameter range (kgf/mm <sup>2</sup> )	Repeatability (kgf/mm <sup>2</sup> )
Tensile strength at break	17.9–24.0	9.0–24.0	1.3
Tensile modulus	434.0–505.0	300.0–505.0	29.6



**Figure 2.** Selected variables represented in the spectrum of PET obtained by ATR, using PLS-Jack-Knife algorithm (●) and using MLR-SPA algorithm (○) to build models for prediction of tensile strength at break.

seen in Figure 1(a), the spectra obtained by direct transmission show regions with saturated bands (hatched areas). Thus before building the models, these regions, had been excluded from the data set. The regions removed are the vibrations associated to the OCO ester group.

### Mechanical Tests

The mechanical tests were performed with films collected from different batches. The range of variation for each property is presented in the first column on Table I. As the production process was under control, the range of variation of the properties of the polymers produced was not wide enough to build reliable models. As recommended in ASTM 1655-05, the range for the property should be at least five times the standard deviation of the reproducibility for the reference analysis. To solve this problem, 48 industrial samples were exposed to gamma radiation (25, 60, 120, 240, and 500 kGy), to extend the range of

**Table II.** Root Mean Square Error of Cross Validation (RMSECV), Root Mean Square Errors of Prediction (RMSEP), Correlation (*R*), the Number of Factors (*n*) and Variables (*m*) for PLS and MLR Models Obtained with Preprocessed ATR Spectra of PET Samples

Preprocessing	PLS				MLR			
	Calibration	Prediction			Calibration	Prediction		
	RMSECV (kgf/mm <sup>2</sup> )	RMSEP (kgf/mm <sup>2</sup> )	<i>R</i>	<i>n</i>	RMSECV (kgf/mm <sup>2</sup> )	RMSEP (kgf/mm <sup>2</sup> )	<i>R</i>	<i>M</i>
None	1.6	1.5	0.91	7	2.1	2.4	0.70	10
Smooth	1.7	1.3	0.92	7	2.1	2.3	0.70	11
SNV	1.6	1.3	0.91	11	2.4	2.0	0.72	6
Derivative	1.5	1.3	0.93	6	1.7	2.3	0.74	9
MSC	1.9	1.6	0.88	7	2.1	2.1	0.75	14
Smooth+ MSC	1.8	1.5	0.88	7	1.8	1.9	0.78	12
Derivative + MSC	1.8	1.4	0.92	8	1.7	2.3	0.74	9
Derivative + SNV	1.8	1.4	0.90	9	2.1	1.5	0.83	12
Smooth + SNV	1.7	1.3	0.91	5	2.0	1.7	0.78	11

**Table III.** Root Mean Square Error of Cross Validation (RMSECV), Root Mean Square Errors of Prediction (RMSEP), Correlation ( $R$ ), the Number of Factors ( $n$ ), and Variables ( $m$ ) for PLS and MLR Models Obtained with Preprocessed Direct Transmission Spectra of PET Samples

Preprocessing	PLS				MLR			
	Calibration	Prediction			Calibration	Prediction		
	RMSECV (kgf/mm <sup>2</sup> )	RMSEP (kgf/mm <sup>2</sup> )	$R$	$n$	RMSECV (kgf/mm <sup>2</sup> )	RMSEP (kgf/mm <sup>2</sup> )	$R$	$m$
None	1.2	1.1	0.91	7	1.2	1.8	0.82	21
Smoothing	1.3	1.2	0.91	8	1.4	1.5	0.83	12
Derivative	1.2	1.1	0.92	7	1.6	1.6	0.87	14
MSC	1.3	1.1	0.93	10	1.4	1.5	0.89	15
SNV	1.2	1.0	0.94	7	1.7	2.2	0.72	12
Smoothing + SNV	1.2	1.1	0.93	8	1.4	1.5	0.83	12
Derivative + SNV	1.3	1.1	0.93	6	1.6	2.3	0.71	11
Smoothing + MSC	1.2	1.1	0.92	7	1.4	1.8	0.78	13
Derivative + MSC	1.4	1.2	0.90	15	1.9	2.2	0.67	9

variation of the mechanical properties under study, without losing the main polymer features. The extended range is presented in the second column on Table I. The values of the standard deviation (intra laboratorial reproducibility), for the reference method were used to evaluate the predictive ability of the method (third column on Table I).

#### Determination of Tensile Strength at Break with ATR Spectra

Table II shows the values of RMSECV (root mean square error of cross validation), RMSEP, the correlation coefficient of the predicted versus reference values ( $R$ ), the number of factors ( $n$ ) for PLS models, and the number of variables ( $m$ ) for the MLR models to compare the performance of some preprocessing techniques applied to the ATR spectra of PET samples. When smoothing or derivation was used, the values presented are the best results obtained after testing different window sizes.

The PLS model built using the spectra processed with smoothing (window size of 9 points) and SNV simultaneously had the lowest RMSEP (1.3 kgf/mm<sup>2</sup>), high correlation (0.91) and needed the lowest number of factors (5) for the model construction. For the MLR models, the pretreatment that originated in the model with smaller RMSEP (1.5 kgf/mm<sup>2</sup>) and had the highest correlation (0.83) was the derivation (window size of 9 points) associated with SNV. This model was built with the 12 most informative spectral variables selected using the SPA algorithm.

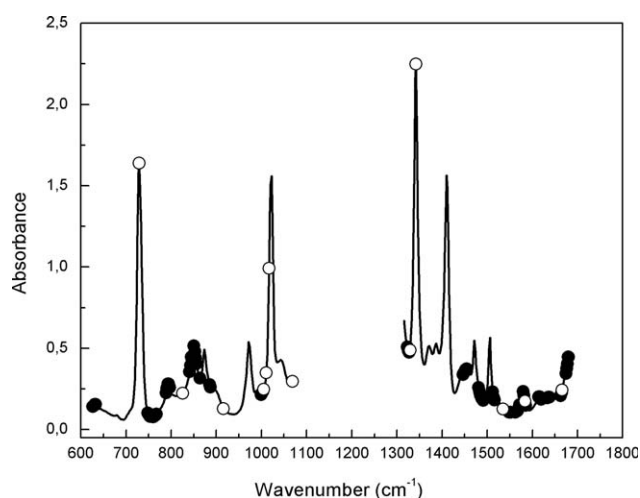
The  $F$ -test was carried out to compare the RMSEP values of the best models for PLS (1.3 kgf/mm<sup>2</sup>) and MLR (1.5 kgf/mm<sup>2</sup>). Those values were considered statistically equivalent at a confidence level of 95% ( $F_{(29,29,0.95)} = 1.9$  and  $F_{\text{calculated}} = 1.3$ ). The RMSEP values for both models are similar to the standard deviation of the reference method.

Figure 2 shows the variables selected using the Jack-Knife algorithm (○) and the most significant variables selected by the SPA (●) for the models mentioned above. There is a preference for regions where there are vibrations of the OCO ester group (1264, 1245, and 1016 cm<sup>-1</sup>), CH aromatic vibrations (1016 and 724 cm<sup>-1</sup>), and C=C aromatic vibrations (1471 and 1507 cm<sup>-1</sup>).

#### Determination of Tensile Strength at Break with Direct Transmission Spectra

Table III represents the results of the models constructed using spectral data obtained by the direct transmission technique. The values of RMSECV, RMSEP, the correlation coefficient of the predicted versus reference values ( $R$ ), the number of factors ( $n$ ) for PLS models, and the number of variables ( $m$ ) for the MLR models have been shown to compare the performance of some preprocessing techniques. When smoothing or derivation was used, the values presented are the best results obtained after testing different window sizes.

The PLS model built using the spectra processed with derivative (window size of 9 points) and SNV simultaneously had the lowest RMSEP (1.1 kgf/mm<sup>2</sup>), high correlation (0.93) and used the lowest number of factors (6). In relation to the MLR, models constructed with smoothed spectra and with spectra treated with SNV associated with smoothed, there was an identical performance, with 1.5 kgf/mm<sup>2</sup> as the lowest RMSEP value and



**Figure 3.** Spectrum of PET samples obtained by direct transmission with the variables selected by the PLS-Jack-Knife Algorithms (●) and MLR-SPA (○) for the construction of models for the tensile strength at break.



**Table IV.** Root Mean Square Error of Cross Validation (RMSECV), Root Mean Square Errors of Prediction (RMSEP), Correlation ( $R$ ), and the Number of Factors ( $n$ ) for PLS Model Obtained with Preprocessed ATR and Direct Transmission Spectra of PET Samples

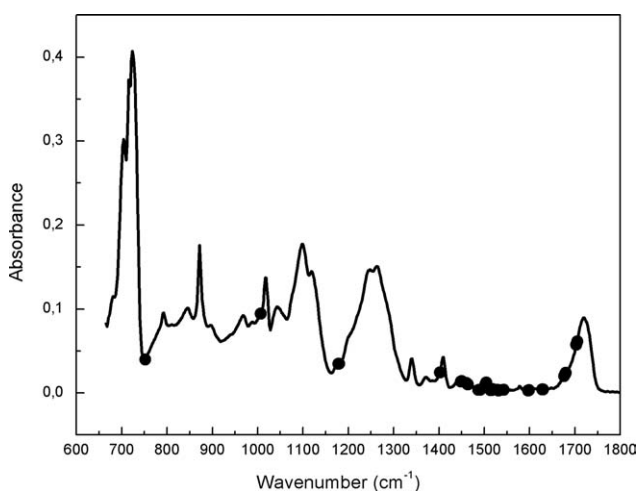
Préprocessing	PLS							
	ATR				Direct transmission			
	Calibration	Prediction		$n$	Calibration	Prediction		$n$
RMSECV (kgf/mm <sup>2</sup> )	RMSEP (kgf/mm <sup>2</sup> )	$R$	RMSECV (kgf/mm <sup>2</sup> )		RMSEP (kgf/mm <sup>2</sup> )	$R$		
Derivative	29.4	30.1	0.80	9	31.1	43.9	0.50	7
MSC	39.6	51.8	0.49	7	31.7	30.6	0.62	9
SNV	31.7	39.5	0.75	5	35.0	32.4	0.57	6
Derivative + SNV	39.3	46.9	0.66	6	32.6	28.6	0.72	10
Smooth + MSC	41.2	52.0	0.24	7	38.8	29.3	0.73	7

0.83 as the correlation. Both models were built using 12 factors (or variables). According to an  $F$ -test at a confidence level of 95%, these three models are statistically equivalent ( $F_{30,30,0.95} = 1.9$  and  $F_{\text{calculated}} = 1.9$ ). These RMSEP values were similar to the precision (1.3 kgf/mm<sup>2</sup>) of the reference method.

Figure 3 shows the variables selected by the Jack-Knife and SPA algorithms. The discontinuity observed in Figure 3 corresponds to the regions with saturated bands removed before model building. As expected from the results obtained using ATR, variables corresponding to CH aromatic vibrations (1016 and 724 cm<sup>-1</sup>) and C=C aromatic vibrations (1471, 1507, and 1580 cm<sup>-1</sup>) were selected.

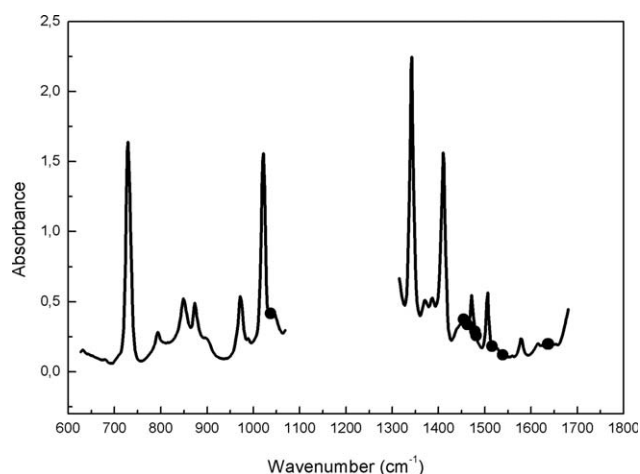
#### Determination of the Tensile Modulus with ATR and Direct Transmission Spectra

Table IV shows the results for the PLS models. The MLR models did not present satisfactory results, and therefore, they have not been shown. MLR models depend on the selection of the variables and cannot deal with non linearities as PLS models. These aspects may have influenced the poor performance of these models.

**Figure 4.** Spectrum of PET samples obtained by ATR the variables selected by the Jack-Knife algorithm (●) for the construction of models to determine the tensile modulus.

For the spectra obtained using the ATR technique, the model with the lowest RMSEP (30.1 kgf/mm<sup>2</sup>) and the highest correlation (0.80) is the one constructed using the derivative spectra (window size of 9 points). For the spectra obtained by direct transmission, the best model was the one built with the spectra processed with smoothing combined with MSC. This model had low RMSEP (29.3 kgf/mm<sup>2</sup>), higher correlation (0.73) and used 7 factors to construct the model. The gamma radiation was not as effective in extending the range of variation of the tensile modulus as it was for the tensile strength at break, and this is reflected in lower  $R$  values when compared with those obtained for the tensile strength at break. However, it was possible to construct PLS reliable models to determine this property, with RMSEP values similar to the precision of the reference method (29.6 kgf/mm<sup>2</sup>).

Figures 4 and 5 show the variables selected by the Jack-Knife algorithm for spectral data obtained by ATR and direct transmission, respectively. The discontinuity observed in Figure 5 corresponds to the regions with saturated bands removed before model building. Figure 4 illustrates the selected variables which correspond to vibration of the OCO ester group (1720 cm<sup>-1</sup>),

**Figure 5.** Spectrum of PET samples obtained by direct transmission with the variables selected by the Jack-Knife algorithm (●) for the construction of models to determine the tensile modulus.

CH aromatic vibration ( $1016\text{ cm}^{-1}$ ), and C=C aromatic vibrations ( $1471$ ,  $1507$ , and  $1580\text{ cm}^{-1}$ ). For the direct transmission data (Figure 5), variables corresponding to the vibrations of CH aromatic ( $1016\text{ cm}^{-1}$ ) and C=C aromatic ( $1471$  and  $1507\text{ cm}^{-1}$ ) have been selected.

## CONCLUSIONS

MIR spectroscopy associated with multivariate calibration has proved to be effective in determining the tensile strength at break and tensile modulus of PET films. For tensile strength at break, both regression techniques used, PLS (Partial least square) and MLR, showed similar results with RMSEP similar to the repeatability of the conventional method used to determine these mechanical properties ( $1.3\text{ kgf/mm}^2$ ). For tensile modulus, PLS models showed better performance, resulting in RMSEP values similar to the precision of the reference method ( $29.6\text{ kgf/mm}^2$ ).

The two techniques for spectra acquisition used (ATR and direct transmission) resulted in reliable models for predicting these mechanical properties. Therefore, any one of them could be applied to industrial quality control. Direct transmission technique, however, is the simpler alternative, not requiring a specific accessory.

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