

Determination of Moisture Content in Nylon 6,6 by Near-Infrared Spectroscopy and Chemometrics

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ABSTRACT: The effects of moisture on the morphology and mechanical properties of polyamides have been extensively studied by a number of researchers. However, the assessment of water content in the resins has been carried out by thermal or thermogravimetric methods, which are destructive. In the present work partial least-squares (PLS) calibration models based on near-infrared (NIR) spectroscopy were produced in order to predict the moisture content of nylon 6,6. Differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and the loss-on-drying (LOD) method were used as reference methods. TGA, LOD, DSC, and NIR analysis were performed in parallel, and the obtained data were used for multivariate calibration purposes. Data pretreatment techniques such as derivation and

multiplicative scattering correction (MSC) successfully eliminated the baseline offset present in the raw spectra and compensated for differences in thickness and light scattering of the analyzed samples. Calibration models were validated by full cross validation with the help of a test set. A comparison of the prediction ability of PLS models based on pretreated data was also done. NIR spectroscopy is a rapid and nondestructive method for the determination of moisture in recycled nylon. The moisture content can be predicted with a RMSEP = 0.05 wt %. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 2165–2170, 2003

Key words: moisture; nylon 6,6; NIR; TGA; DSC; LOD; PLS

INTRODUCTION

Nowadays there is an increasing need for better quality control of polymers and polymeric composites in order to improve product quality and reduce production costs and waste materials. Plastic recycling, in particular, requires quick and nondestructive quality methods to guarantee good properties of the recyclate. Measurements need to be performed rapidly and to give precise information on the parameters leading to higher-quality products.

Nylons are considered hydrophilic polymers but have different water affinities according to their structure.^{1,2} At room temperature and above, water generally acts as an effective softener or plasticizer, facilitating molecular chain movement by reducing the intermolecular forces of the polymer chain among themselves³; this decreases the glass-transition temperature (T_g) and stiffness but increases flexibility.

The most common technique for determining the absorbed moisture content in nylon is thermal analysis, such as differential scanning calorimetry (DSC), the loss-on-drying (LOD) method and thermogravimetric analysis (TGA). Although these methods require little sample preparation, they are time consum-

ing and destructive; consequently, they cannot be used for at on-line analysis.

Chemical methods such as Karl–Fischer titration are also used for this purpose. The water is removed from a sample by heating it and passing dry nitrogen gas over it, which picks up the water and is then bubbled through moisture-free methanol to transfer the moisture into it. This solution is titrated with Karl–Fischer reagent for determining the mass of water driven off. Knowing the mass of the sample, it is possible to determine the water content present. This technique has the same disadvantages as the ones mentioned before; in addition, the use of toxic solvents makes sample handling hazardous and troublesome.

The introduction of chemometric methods and light-fiber optics has opened the possibility of using NIR spectroscopy as a rapid, nondestructive method, providing ease of sampling, low cost, and high reliability. NIR spectroscopy can be used in a laboratory or in process control. Light-fiber cables can be used to link the plant and the safe-control room, allowing the extraction of information without having to physically remove samples from the processing line.⁴

NIR is based on measurements of light absorbed by the sample when it is exposed to electromagnetic radiation in the range from 780 nm ($12,820\text{ cm}^{-1}$) to 2500 nm (4000 cm^{-1}). Qualitatively, this is the region between the visible red and the highest frequency used in conventional midinfrared. Light in this range can be

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used to excite overtone and combination transitions of molecular vibrations and electronic transitions of highly conjugated systems. An overtone of a vibrational mode occurs when a single photon excites a molecular vibration from the ground state to a second or higher excited state. A transition from the ground state to the second excited state is called the first overtone transition, a transition from the ground state to the third excited state is known as second overtone transition, and so on. A combination band occurs when a single photon excites two or more different molecular vibrations. Only combinations and overtones involving higher-frequency fundamentals are strong NIR absorbers, that is, CH, OH, NH, C=O, and COOH. Other vibrations have only higher-order overtone bands in the NIR region, which are very weak compared with the first and second overtones. For a given molecule many active overtone and combination bands might be present in the NIR region, giving, as a result, a spectrum with a large number of overlapping bands, making spectral interpretation difficult. The overtone and combination bands are approximately 10–100 times less intense than the fundamental bands of the midregion. This allows (requires) the use of relatively large path lengths. Thick samples (from 1 mm to several centimeters) can be analyzed by NIR transmission spectroscopy.⁵

An isolated water molecule has three modes of vibration: the symmetric stretch (ν_1), the bend (ν_2), and the antisymmetric stretch (ν_3). These three vibrations absorb strongly in the fundamental part of the IR spectrum (mid-IR), which spans from 400 to 4000 cm^{-1} at 3450–3700 cm^{-1} , 1595–1650 cm^{-1} , and 3550–3750 cm^{-1} , respectively. Overtones (such as $2\nu_1$ at 6900 cm^{-1}) and combination bands (such as $\nu_2 + \nu_3$ at 5160 cm^{-1}) of these bands are observed in the near-infrared.^{4,6}

Several researchers^{7–9} have used mid-IR for studies of water and other liquids in polymer films. Several techniques are applied in this region, that is, attenuated total reflection (ATR), specular reflectance, and transmission IR. Water diffusion in polymer films has been successfully studied by analyzing the absorbance change of a peak at 3350 cm^{-1} , which characterizes the stretching of the OH group in this spectral region. Unfortunately, these methods work well only for analysis of thin films.

In the present study partial least-squares (PLS) calibration models based on NIR spectral were produced in order to predict the moisture content in nylon 6,6. TGA, LOD, and DSC were used as reference methods.

EXPERIMENTAL

Materials

Polyamide 6,6, Zytel E101L (injection-molding grade), was provided by DISTRUPOL Nordic AB, Sweden. The

resin was injection-molded into dumbbells according to ASTM standard D-638 using a Battenfeld Plus 250/50 equipped with a single screw (diameter = 2.2 cm, L/D = 16). The barrel temperatures were 285°C in the first heating zone, 290°C in the second, and 100°C in the mold. The tensile bars were subsequently re-ground, dried in an oven at 100°C for 15 h, and injection-molded.

The samples were immersed in a water bath at 60°C \pm 1°C. A separation of approximately 3 cm between the samples was provided to permit the water to diffuse freely and prevent surface contact. The specimens were removed periodically at different times, blotted, and conditioned in an inert atmosphere for 1 h before analysis. Thermal and NIR analysis were performed, and the obtained data were used for multivariate calibration purposes.

ANALYTICAL METHODS

Thermal gravimetric analysis (TGA)

A TGA instrument, TGA/SDTA 851^e from Mettler Toledo (Stockholm, Sweden), provided with a horizontal balance was used to assess the moisture uptake of the specimens. The samples were cut transversally from the narrow sections of the tensile bars with a scalpel. Then 30–40 mg of the sample was placed in an alumina pan (70 μL) and heated isothermally at 130°C for 10 h under a nitrogen stream of 50 mL/min. The change in weight was continuously registered. The alumina pan was burned up at 1000°C for 10 min under an oxygen atmosphere after each run in order to eliminate impurities.

Differential scanning calorimetry (DSC)

Thermal analysis was performed on a Mettler Toledo differential scanning calorimeter, model DSC 820, under a nitrogen atmosphere. The instrument was calibrated with indium standard. Aluminum pans with a capacity of 40 μL were conditioned in a humid environment in order to eliminate the formation of aluminum hydroxide in their inner surface during the scanning cycle. To determine the intrinsic water content, about 15 mg of the sample was accurately weighed to a sensitivity of 0.001 mg. The pans were sealed and pierced to allow the moisture to evolve. Samples were heated from 25°C at a heating rate of 10°C/min. An endothermic deviation in the baseline because of the vaporization of water was observed. The sample was heated until no deviation in the baseline was detected. This occurred at 250°C. The dried samples were reweighed after the heating cycle. Samples were analyzed in triplicate.

Loss on drying (LOD)

Samples of approximately 90 g were cut transversally from the narrow sections of the tensile bars with a scalpel and accurately weighed in the microbalance mentioned above. They were immediately placed in a universal oven at 130°C. The samples were periodically removed and weighed until a constant weight was reached. Samples were analyzed in triplicate.

Near-infrared spectroscopy (NIR)

Near infrared spectra were collected in transmission mode with a Perkin Elmer Spectrum 2000 equipped with a tungsten-halogen lamp with a quartz envelope and a deuterad triglycine sulfate (DTGS) detector. Sixty-four scans were averaged at a 4 cm⁻¹ resolution in the range of 4500–9000 cm⁻¹. Three samples were analyzed, and spectra were collected in five sections (five replicates) of each sample.

Unscrambler 4.0 from Camo AS, Norway, was used for multivariate data analysis. Principal component analysis (PCA) was performed on the spectral data and partial linear squares (PLS) calibration was carried out on raw and pretreated data. The spectra of the samples were averaged in order to increase the signal to noise (S/N) ratio and reduce experimental error. Two methods of data pretreatment were applied to compensate for possible physical differences among the samples, such as sample thickness, shape and light scattering, multiple scattering correction (MSC), and second derivative. The calibration models obtained by MSC were validated by full cross validation. Savitzky-Golay convolution derivation using a third polynomial order function and 25 data points were used to obtain the second derivative of the spectral data. The best calibration model was also validated with the help of a test set consisting of six samples of different water content.

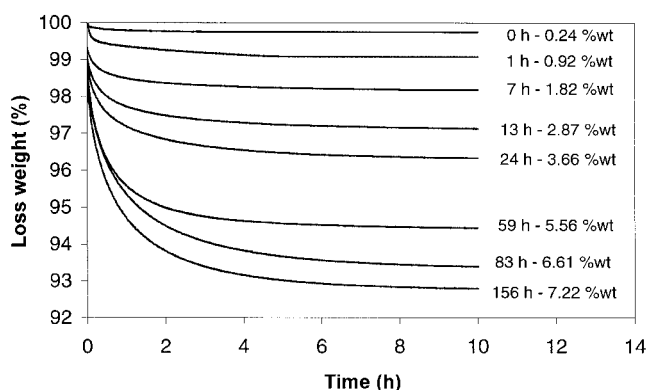


Figure 1 TGA thermograms of recycled nylon 6,6 conditioned at 60°C with different water contents.

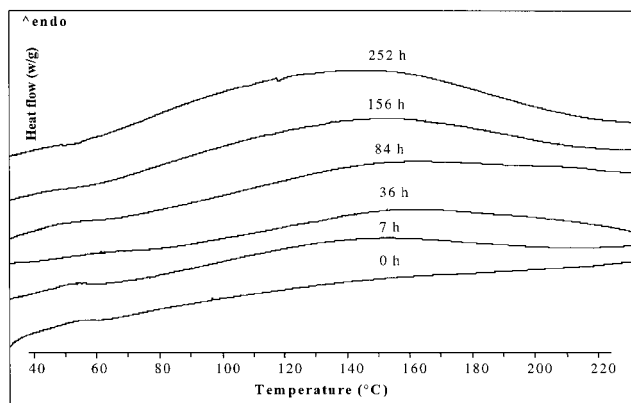


Figure 2 DSC thermograms of recycled nylon 6,6 immersed in water at 60°C for different time periods.

RESULTS AND DISCUSSION

TGA, DSC, and LOD were used for monitoring the moisture content in samples of nylon 6,6 conditioned in water at 60°C for different time periods until equilibrium was reached. NIR measurements in transmission mode were parallel-performed on the nylon specimens. Subsequently, the spectral data were used to obtain calibration models for the prediction of moisture content from NIR spectra. The water content values obtained from thermal methods were used as reference methods for calibration.

Figure 1 depicts examples of TGA thermograms of nylon samples containing different amounts of water. The samples have been immersed in water at 60°C for different time periods. It can be observed that a total loss of moisture under isothermal conditions requires long running times. Up to 10 h was necessary to evolve completely the water from the resin. Minimal sample preparation, high sensitivity, and accuracy characterize the method. However, trouble might be caused by only small amounts of a sample being analyzed if the analyzed sample is not representative of the bulk. Furthermore, the destructive nature and low throughput of the method make it impossible for the method to be used for rapid at- or on-line determination of moisture uptake in polymers.

Figure 2 shows DSC thermograms for a dry sample, several saturated samples, and a supersaturated sample. An endothermic broad peak characteristic for water can be observed for the saturated samples. Because of the high enthalpy of vaporization of water, 2257 J/g,¹⁰ the presence of small amounts of it can be readily detected. DSC has been successfully utilized for determination of the intrinsic water content.^{11–13} Even though the samples can be analyzed in a rapid manner, DSC remains a destructive technique.

The LOD method also provided very satisfactory results. Nevertheless, this method is tedious and time consuming because samples need to be removed periodically for weighing.

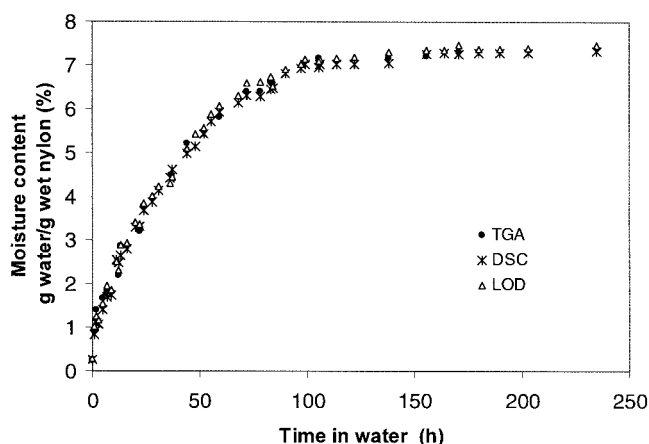


Figure 3 Comparison of moisture content measured by DSC, TGA, and the LOD method for recycled nylon 6,6 immersed in water at 60°C.

The moisture content was determined as follows:

$$\text{Moisture content (\%)} = \frac{w_{\text{wet}} - w_{\text{dry}}}{w_{\text{wet}}} \cdot 100$$

where w_{wet} is the weight of the polymer before drying and w_{dry} is the weight of the dry polymer.

Figure 3 displays the water contents obtained by TGA, DSC and LOD. The difference in the resulting data from these three techniques was minimal, approximately 0.08%.

Figure 4(a,b) depicts the NIR spectra of several nylon samples with different moisture contents before and after MSC treatment. The intensity of two peaks, one at 6880 cm^{-1} and the other at 5150 cm^{-1} , increased proportionally to the water content. These peaks are well defined and characterize the first overtone of the symmetric stretching and the combination band of the antisymmetric stretching and bending of the OH group of water.

Partial least-squares (PLS) calibration was performed on raw, derived, and MSC-pretreated NIR data.¹⁴ In all cases two principal components (PC) described the whole variation in the spectral data, which simultaneously best described the moisture content of the samples in the calibration set. Figure 5 depicts the score plot for the PLS model obtained from MSC-pretreated data using DSC results as the reference method. The plot gives information about patterns in the samples. The score plot for (PC1, PC2) is especially useful because these two components summarize more variation in the data than any other pair of components. The closer the samples are in the score plot, the more similar they are with respect to the two components concerned. Conversely, samples far away from each other are different from each other.

The first component (PC1) describes approximately 85% of the variation in the spectral data; therefore, it

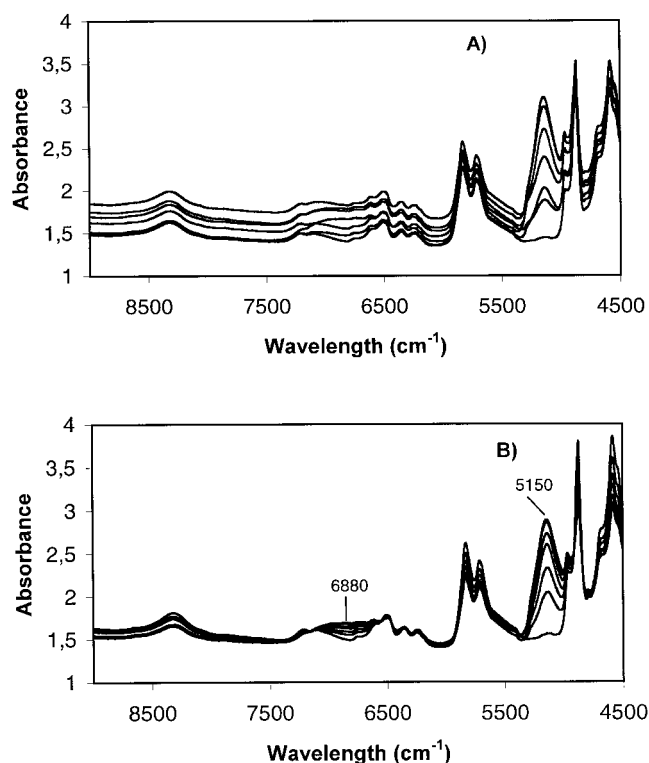


Figure 4 (a) Raw NIR spectra and (b) MSC-treated spectra in the 4500–9000 cm^{-1} region of recycled nylon 6,6 conditioned at 60°C.

can be directly related to the water content, whereas the second component (PC2) represents some other physical property inherent in the resin. The exposure of nylon to water causes morphological changes in the polymeric matrix. Low score values in PC1 correspond to low moisture contents in the resin.

The second derivative was also tested as a pretreatment method in order to eliminate the baseline offset from variations in sample thickness and/or light scattering effects. All the models were validated by random cross validation. Table I shows a detailed list of the root mean square errors of prediction (RMSEP)

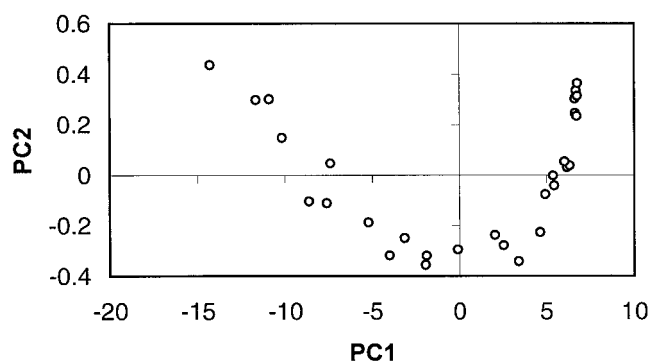


Figure 5 Score plot of the two first PC factors for the PLS model obtained from MSC-pretreated data using DSC as the reference method.

TABLE I
Root Mean Square Errors of Prediction (RMSEP) and Correlation Coefficients (R^2) of PLS Models Obtained with Different Data Pretreatment and Different Reference Methods

Calibration model	RMSEP	R^2
PLS model on raw data using DSC as reference method	0.054899	0.999093
PLS model on MSC pretreated data using DSC as reference method	0.050003	0.999745
PLS model on second derived pretreated data using DSC as reference method	0.057672	0.999298
PLS model on raw data using TGA as reference method	0.059363	0.999092
PLS model on MSC pretreated data using TGA as reference method	0.0599	0.999291
PLS model on second derived pretreated data using TGA as reference method	0.05417	0.999004
PLS model on raw data using LOD as reference method	0.054582	0.999845
PLS model on MSC pretreated data using LOD as reference method	0.049421	0.999828
PLS model on second derived pretreated data using LOD as reference method	0.052545	0.999087

and correlation coefficients (R^2) for the different methods. The RMSEPs obtained using TGA, DSC, and LOD as reference methods varied only slightly. This confirms the equivalence of these methods for water uptake assessment. Prediction of the water content in the specimens of the test set was performed with the PLS calibration model obtained from the MSC-corrected spectral data, using LOD as the reference method.

Figure 6 shows the regression coefficient plot of the calibration model from MSC-pretreated data based on DSC. Regression coefficients summarize the relationship between all predictors and a given response. For PCR and PLS, the regression coefficients can be computed for any number of components. This plot shows the regression coefficients for one particular response variable—water content—and for a model with a particular number of components, two in this case. Each wavelength defines one point of the line. Because the spectroscopic data have been weighted (centered and standardized), the regression coefficients take these weights into account, and all predictors have been brought back to the same scale, the coefficients show the relative importance of those variables in the model. Predictors with a large regression coefficient play an important role in the regression model; a positive coefficient shows a positive link with the re-

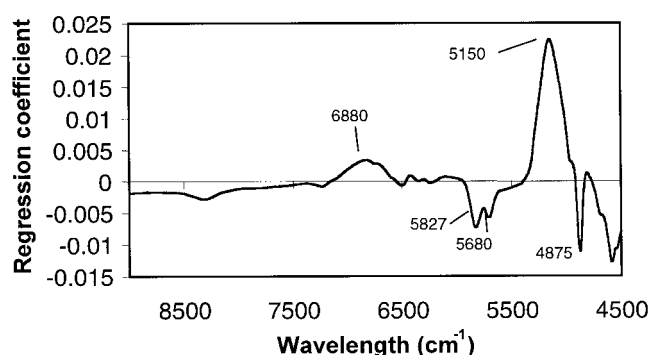


Figure 6 Regression coefficients of the PLS model obtained from MSC-pretreated data using DSC as the reference method.

sponse, a negative coefficient a negative link. Predictors with a small coefficient are negligible.

It can be seen that the wavelengths at 6880 cm^{-1} and especially 5150 cm^{-1} have a very high positive influence on the model. As mentioned above, these two bands represent combinations of bending and stretching modes of the OH group in the midspectral region. The bands at 5827 and 5680 cm^{-1} , which are attributed to the first overtone of, respectively, the asymmetric and symmetric stretching of CH_2 , and the band at 4875 cm^{-1} (a combination of NH stretching and amide III) have a negative influence on the model. The negative influence of these bands may be a result of the weaker strength of the hydrogen bonds to N—H in the presence of water. It has been observed that the intensity of this band decreased when the water content is increased. Water reduces molecular interaction between nylon chains, increases free volume by pushing polymer chains apart, and disrupts the order, in this way producing changes in the crystallinity and T_g of nylon 6,6. The intensities of CH_2 and NH bands have been used by Chaupart et al.¹⁵ to calculate water accessibility in different polyamides. Regions that had very little or no influence on the model were not taken into account in the final PLS calibration models.

The PLS calibration model for MSC-pretreated data using LOD as the reference method was also validated with the help of a test set consisting of six samples. Figure 7 shows the calibration model. The samples of the validation set were predicted with an averaged deviation of 0.05 wt %.

All the experiments were carried out on nylon, which was reprocessed twice; it was observed that further reprocessing induced strong darkening of the material, making the spectroscopic analysis more difficult because the S/N ratio decreased notably as a result of the high absorptivity of the dark specimens. Nevertheless, because of the high resolution and intensity of the peaks, characteristic of water in the NIR region, this method can be reliably used as an in-line/on-line method for moisture measurement in either

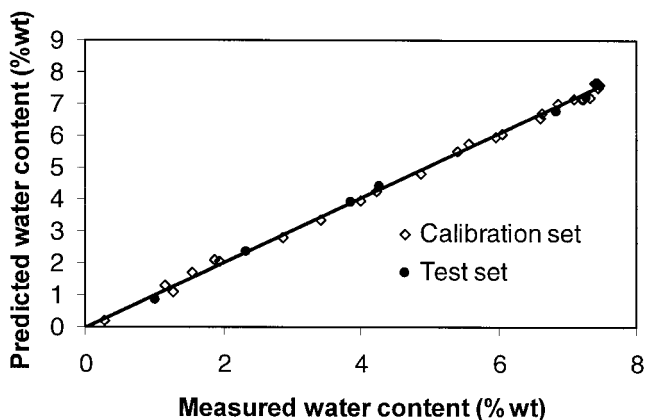


Figure 7 PLS calibration model obtained from MSC-pretreated data using LOD as the reference method.

virgin or recycled nylon, provided the analyte is not too dark or black.

CONCLUSIONS

NIR spectroscopy is a rapid and nondestructive method for the determination of moisture content in recycled nylon, which can be predicted with an RMSEP of 0.05 wt %. The advantage of nondestructive NIR measurements is being able to subject the testing specimens to another analysis—mechanical tests immediately after the determination of moisture content. The disadvantage of reprocessing (recycling) is having material that turns a dark brownish color after further

reprocessing, making NIR analysis more difficult because dark and black samples absorb all light.

The low absorptivity in the NIR spectral region ($4000\text{--}12,000\text{ cm}^{-1}$) makes it possible to analyze thick samples in transmission mode. Data pretreatment techniques such as derivation and MSC successfully eliminated the baseline offset present in the raw spectra and compensated for differences in thickness and light scattering of the analyzed samples.

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