CLASSIFICATION OF POLYMER RAW MATERIALS BY NEAR-INFRARED OPTICAL SPECTROSCOPY

Analytical method has been developed for classifying polymer raw materials using a near-infrared (NIR) analyzer equipped with a diffuse-reflectance fiber-optic probe.

Nowadays, a vast number of polymer products are manufactured and processed. Therefore, the problem of reliable identification and classification of polymer raw materials and products becomes particular importance. Optical spectroscopic techniques are well-suited to address this issue, particularly vibrational spectroscopy, which relies on measuring the absorption of infrared (IR) radiation. The methods that enable measurements to be conducted outside the chemical lab, i.e. in the field and online conditions, are gaining momentum. Such analysis often involves the development of optical sensor systems (OMS), specialized, out-of-lab analyzers, which can be based, for example, on light-emitting diodes (LEDs). OMS can be incorporated into a production line or implemented as portable, compact devices.

The near-infrared (NIR) region (780-2500 nm) contains the spectral responses of all major functional groups of various polymer molecules, and it has several advantages over the mid-IR region. Thus, NIR spectroscopy allows for the measurement of the spectra of solid samples in diffuse-reflection mode using fiber-optic probes, without the need for sample preparation. The penetration depth of NIR radiation into the sample is up to a few millimeters, which is important for determining the composition of the bulk sample volume, rather than the surface layer only. Analysis times can be as short as a few milliseconds, making it suitable for flow-through analysis in automated systems. These advantages turn NIR spectroscopy into an optimal tool for developing a reliable polymer classification meth. The strong overlap of absorption bands in the NIR region can be successfully overcome by the application of multivariate data analysis, also known as chemometrics, in particular, the principal component analysis (PCA) algorithm.

The following polymers were tested in the study: polyethylene terephthalate (PET), acrylonitrile butadiene styrene (ABS), polypropylene (PP), polycarbonate (PC), and linear low-pressure polyethylene (LLDPE). The samples were in the form of granules produced by extrusion, and they looked like distorted cylinders with a diameter of approximately 3 mm (Fig. 1, left).

Figure 1. A polymer granule placed at the fiber probe tip (left) and the probe with six illuminating and one detecting channel (right).

The measurements were conducted using a NIRQuest NIR-spectrometer (OceanOptics, USA) operating in the wavelength range of 1100-1750 nanometers. The spectral measurements were performed using a diffuse-reflection probe from art photonics GmbH (Berlin, Germany) having six illuminating fibers and one detection fiber (Fig. 1, right). The sample was illuminated by a stand-alone halogen lamp light source (OceanOptics). For measurements, a polymer granule was placed at the probe tip (6 mm in diameter). A 100% reflectance Spectralon® standard was used as a reference sample. Before the analysis, spectral data were normalized using the standard normal variate (SNV) algorithm. To investigate the method feasibility for the polymer recognition, a non-supervised PCA classification algorithm was used. The data analysis was performed in TPT-cloud – the chemometrics software available online at tptcloud.com.

Each polymer was represented by six randomly chosen granules. Each of them was measured three times in different positions. The resulting 90 spectra of the samples are presented in Fig. 2. The NIR spectral regions contain rich chemical information about the structure of the studied polymers. The raw spectra (Fig. 2, top) are affected by the so-called “scatter effect”, which can be essentially eliminated by using SNV-normalization (Fig. 2, bottom). Nevertheless, the absorption signals of functional groups related to different polymers overlap significantly, making it difficult to classify all polymers unambiguously using a single wavelength or spectral interval.

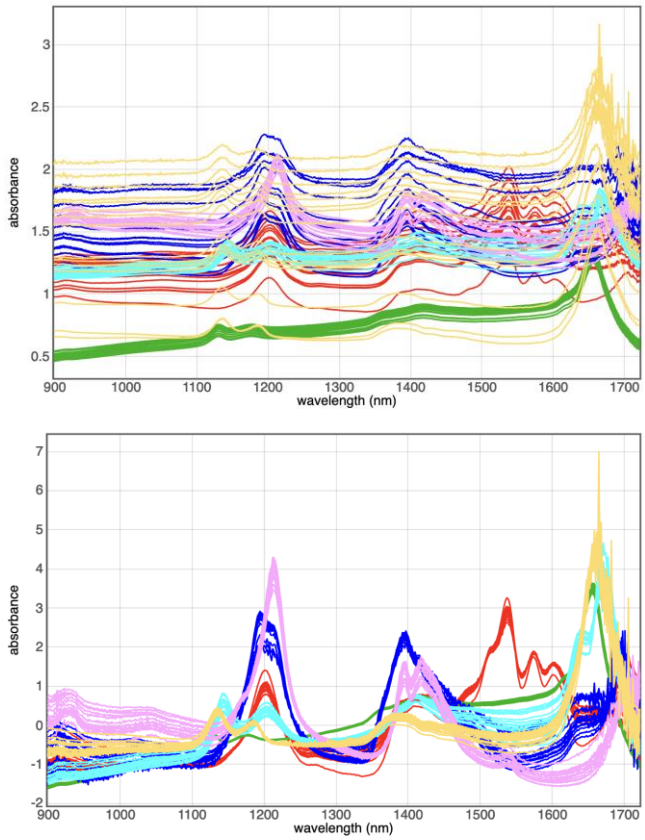

Figure 2. NIR-spectra of PP (yellow), PET (pink), PC (blue), LLDPE (green) and ABS (red): raw data (top); and SNV-normalized (bottom).

Even after applying the SNV normalization, there is still a significant signal overlap and spectral intensity variation within each class of polymers. These factors make traditional classification methods based on a single intensity or peak area impractical. Therefore, we used PCA as a multivariate chemometrics approach for a non-supervised (i.e. data-based) cluster analysis.

The scatter plots of PCA scores are presented in Fig. 3. Each point in PCA scores (also called “sample map”) represents a particular spectral measurement, and the distance between them reflects the respective spectral differences. As can be seen, the spectral method combined with the SNV-preprocessing allows us to unambiguously classify polymers into distinct groups in PC1-PC2 plot (Fig. 3, top), i.e. all polymers in the figure form compact non-overlapping clusters. The PCA-model built on the raw data requires 5 PCs, and the isolated clusters are observed in a plain of PC3-PC5 scores (Fig. 3, bottom). The PCA-results obtained illustrate the fundamental possibility of constructing predictive classification models using NIR spectra in the region 900-1700 nm.

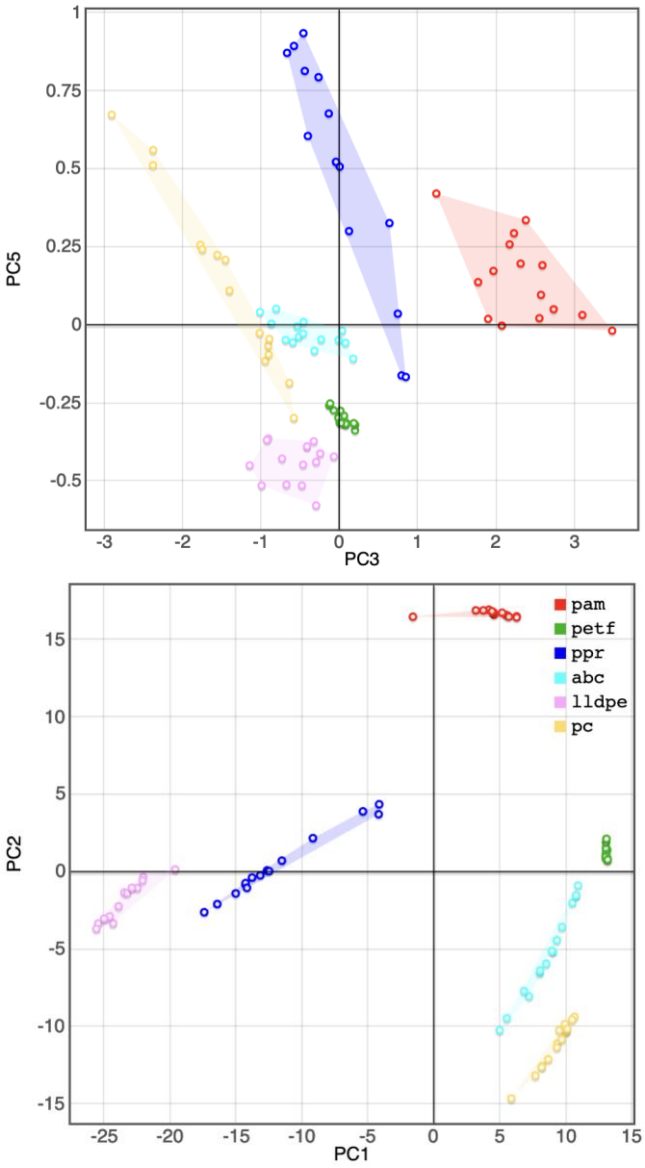

Figure 3. Score plots for the PCA-model built on: raw spectra (top); and SNV-normalized NIR-spectra (bottom).

From the point of view of the further OMS development, it is important that the class separation can be achieved using the raw spectral data without any multivariate preprocessing, such as SNV-normalization.

The chosen spectral region (900–1650 nm) allows the use of conventional class optics and fiber probes, as well as relatively inexpensive LED-radiation sources. which makes it rather practicable for the development of LED-based optical sensor systems.

To conclude, the fiber-probe based NIR spectroscopy up to 1650 nm enables unambiguous classification of the six main polymers under study. This feasibility study using PCA cluster analysis has shown that the chosen spectral region can be used for the development of both a full-featured spectroscopy method and an optical multisensor systems.

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DIN EN ISO 9001:2015
Zertifikat Nr. A1887GER