Application Note AN R529

Chemical Imaging of the Complex Multilayered Structure of Disposable Diapers

Disposable diapers were invented and brought to the market in the middle of the 20th century. Today the market volume for disposable diapers is tens of billions USD.

Starting from a rather easy design the disposable diaper was constantly developed towards the high-tech product which is available nowadays. However, to stay ahead of competitors the producers of diapers seek for innovations that might further improve properties like weight, absorbing capacity and wear comfort.

Modern disposable diapers have a complex multi-layered structure that has to fulfill many different tasks. Typically there is a nonwoven fabric on the inside which transports any fluid towards an adsorbing core, and keeps the skin dry. An additional layer distributes the fluid before it enters the adsorbing material which might be cellulose-based or a polymeric super absorber. On the outside, the diaper is held together by a breathable polymer fabric.

The individual layers are often laminates by itself and contain various materials like a basic polymer, certain fillers and embedded fibers. Additionally adhesive layers bond the different elements to each other.

During the R & D phase it is required to understand and characterize the chemical composition of the new product. Furthermore, the analysis of competition products helps to stimulate own developments. Finally, any failure of the product raises urgent need to find the reason behind the problem.

Keywords	Instrumentation and Software
Disposable Diapers	SENTERRA II Raman Microscope
Multilayer Structures	OPUS Spectroscopic Software
Composite Materials	OPUS SEARCH Spectral Identification Software
Nonwoven Fabrics	Spectral Databases
Chemical Imaging	
Material Identification	

Raman micro-spectroscopy is a very powerful tool to identify the chemical nature both of organic and inorganic material. Due its capability to resolve spatially down to about 1 µm the method allows to generate chemical images that show the distribution of individual components within heterogeneous materials. As the Raman microscopic analysis is performed contact free even soft materials like nonwoven fabrics can be analyzed very accurately.

This application note shows the use of Raman micro-spectroscopy to identify the individual materials which are used in different layers of disposable diapers. Layers and heterogeneously distributed components are visualized by chemical images.

Instrumentation

The SENTERRA II is a compact Raman microscope that combines excellent sensitivity with high resolution and state-of-the-art imaging performance (figure 1).

Due to the high degree of instrumental intelligence the SENTERRA II is a very comfortable and intuitive to use system. Hardware and software are integrally linked. While the operator is guided by the software through the Raman microanalytical workflow, all relevant hardware changes are performed automatically.

For the analysis the multi layered composite film is fixed between the two clamps of a microscopic sample holder. Then the film is cut with a microtome knife to produce a smooth surface of its cross-section. This type of sample preparation can be performed very quickly without specific tools and without special skills.

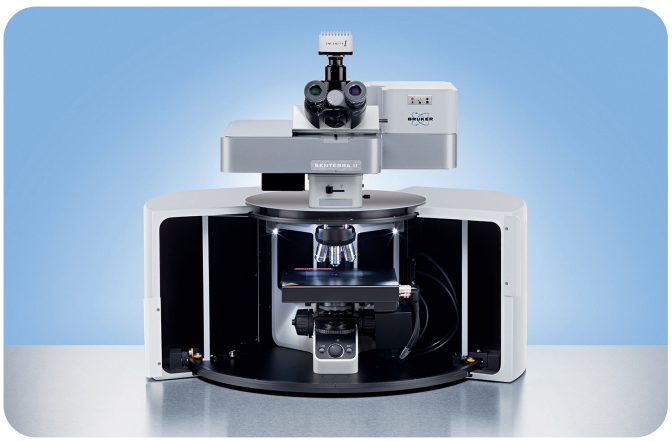

Figure 1: SENTERRA II Raman Microscope

Analysis of the outside layer of a baby diaper

The outside layer of baby diapers shall retain the liquid water which is kept by the absorbers but also be permeable to air and water vapor. Such complex functionality can be accomplished by dedicated polymer laminates.

For the Raman analysis of the laminate the first step within the software guided workflow of the SENTERRA II was the acquisition of visual microscopic images with an 50 x objective. Then the optimal laser excitation was determined by checking the obtained Raman spectra on different positions of the sample using the live spectrum preview. As the laser excitation at 532 nm induced fluorescence at certain positions of the sample, a different parameter set was loaded by a single mouse click, changing the instrument settings automatically to 785 nm. Using this laser excitation with a power of 12 mW resulted in high quality spectra without fluorescence. A 50x microscope objective was used. A line of 210 measurement positions with a step width of 0.55 µm was laid over the cross section of the laminate and then measured automatically (figure 2).

The measured Raman data was evaluated by means of a so-called cluster analysis that groups the spectra according to their similarity. Three different groups of spectra were found, representing the materials which are used in altogether seven layers inside the composite film.

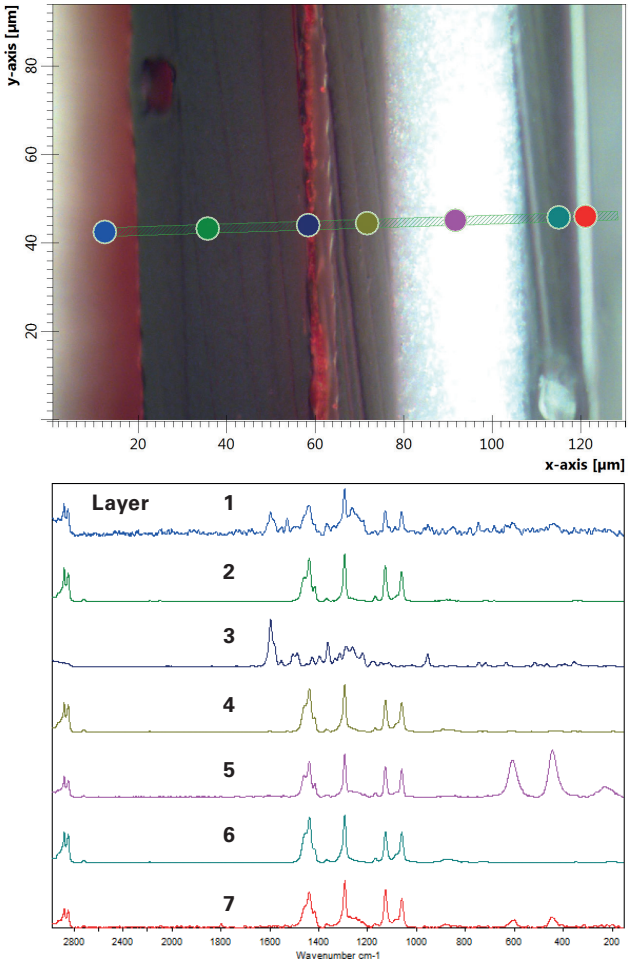

Figure 2: Top: Visual microscopic image of laminate cross-section. The green area indicates the line of measurement points; the spots are individually selected spectra. Below: Spectra measured at the indicated positions.

The identification of the materials was performed by automated search of the measured spectra in Raman spectral libraries. The search result in the upper part of figure 3 shows the clear match of the spectrum which was measured on the layers no. 2, 4 and 6 with a polyethylene spectrum from the library. Obviously the same peaks are also present in the spectra of the two bright layers no. 5 and 7.

Though, additional bands <500 cm^{-1} indicate the presence of further components. By applying the mixture analysis function in the OPUS spectroscopic software the best combination of library spectra is found to match all bands in the sample spectrum. The lower part of figure 3 shows the mixture analysis result which determines the filler titan oxide (polymorphic form: rutile) to be present next to the polyethylene. The "composite spectrum" that is calculated as a sum of the found library hits perfectly matches with the sample spectrum.

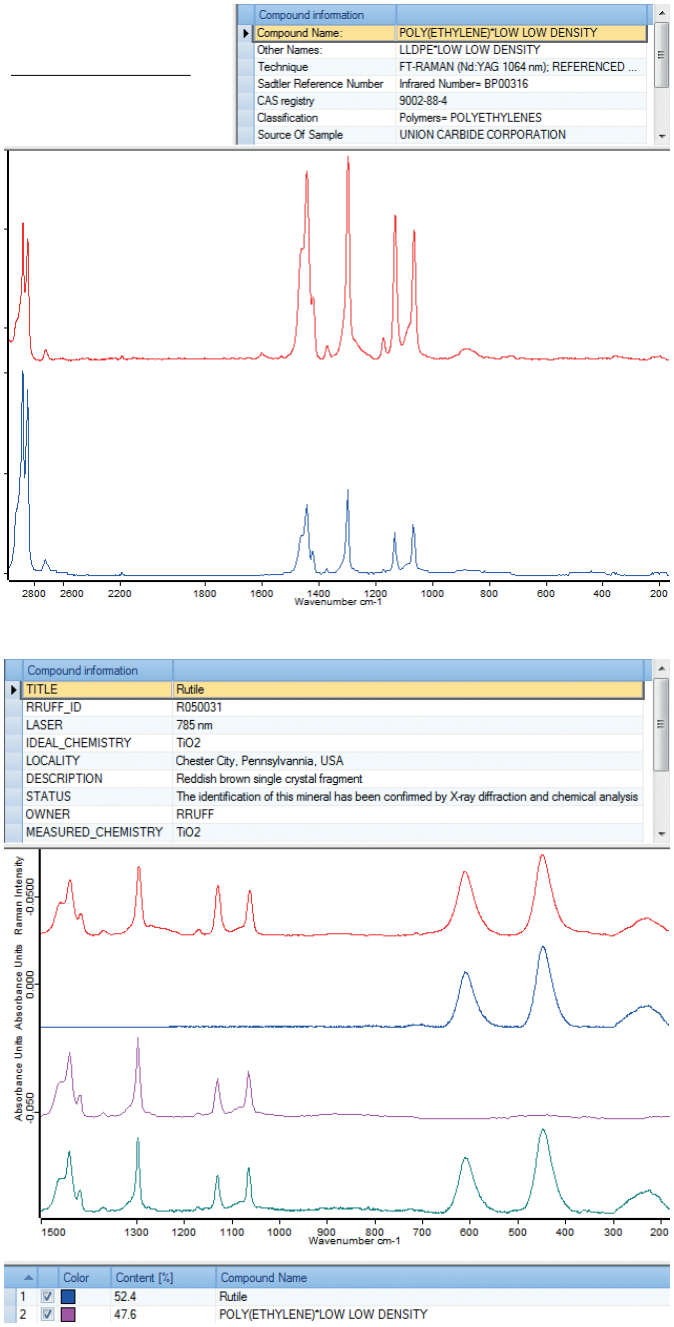

Figure 3: Top: Identification of the spectrum measured on three layers as polyethylene by spectrum search.

The spectra measured on the whitish layers clearly show additional bands. Mixture analysis determines these spectra to originate from TiO_2 filled polyethylene (bottom)

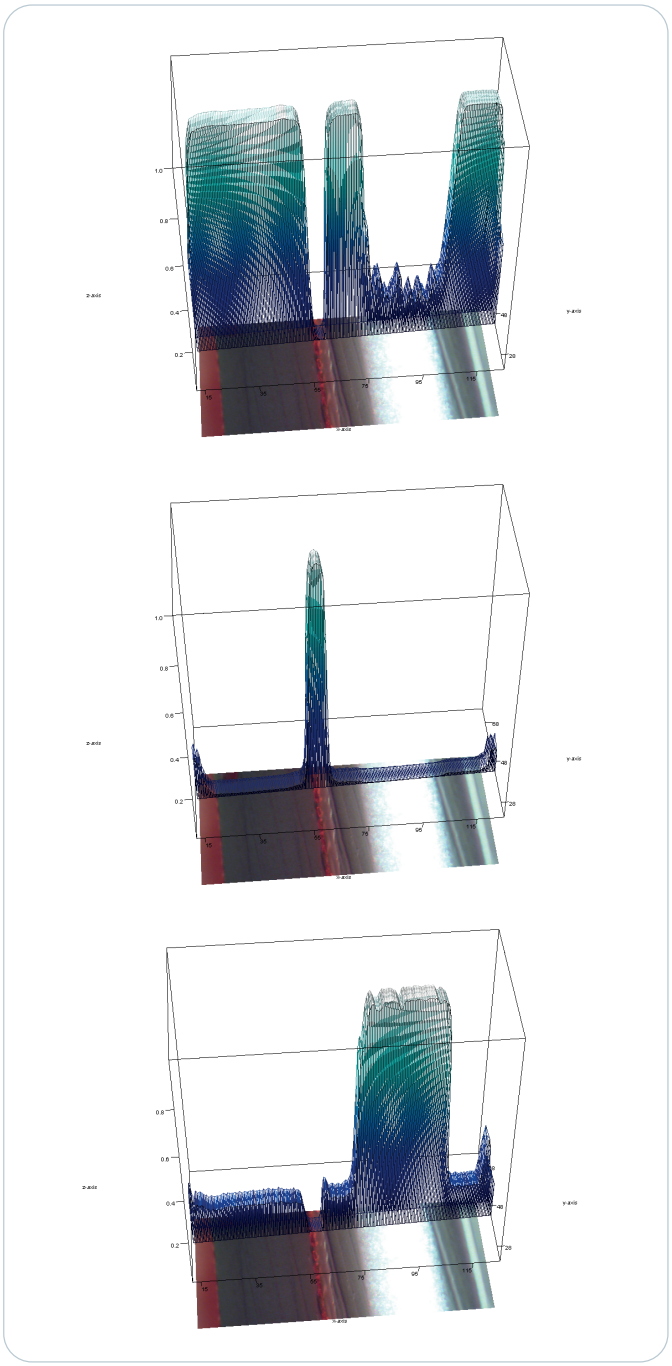

Figure 4: 3D chemical images showing the distribution and thickness of the different layer materials in the laminate. Top: Polyethylene, middle: Red layer, below: TiO_2 filled Polyethylene. The thickness of the layers is determined from left to right with 3 µm, 40 µm, 6 µm, 13 µm, 31 µm, 12 µm, 3µm

The spectra of the red layers are dominated by bands originating from the organic dye compound.

Additionally to the identification the obtained spectral information can also be utilized to generate chemical images of the sample. Figure 4 shows 3D plots that were generated by correlating reference spectra of the three different found materials against the complete line map. High columns with bright colors indicate a strong correlation.

As the sample integrity is preserved by the non-contact nature of the Raman technique the obtained Raman images also allow to determine the diameters of the individual polymer layers. Furthermore the Raman method does not require such demanding sample preparation like optical microscopy, where typically microtome thin sections of the laminates have to be prepared to determine the number and thickness of layers.

Composition of a nonwoven fabric

Nonwoven fabrics are sheets that are manufactured from different fibers which form a porous structure. Such materials are used on the inside of the diaper which is in contact with the skin.

The measurements performed in this example are aimed at identifying the used fiber materials and at showing their distribution. Again the 785 nm laser excitation was found to be most suitable for measuring the sample without disturbing fluorescence. An integration time of 2 seconds/spectrum was applied to obtain high quality Raman spectra on the fluffy surface of this sample. A sample area of about 110 x 300 µm was imaged with a step width of 5 µm.

The presence of two different fiber materials was determined, polypropylene (PP) and poly ethylene terephthalate (PET). By integrating bands that are specific for the two components chemical images of the distribution of the two materials were generated (figure 5). The visual microscopic image overlaid with the Raman image now shows a chemical contrast in addition to the visual one.

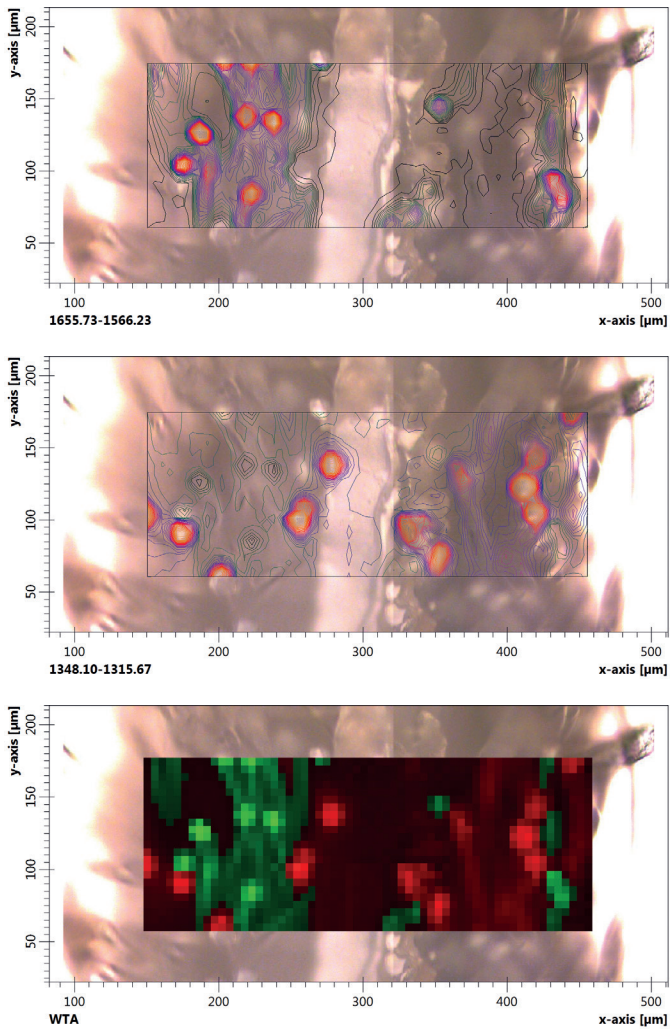

Figure 5: 2D chemical images overlaying the visual microscopic image of a cross-section of the nonwoven inside layer in a diaper. The distribution of the different polymer fibers is shown: on top PET, PP in the middle, both combined below (PET shown in green, PP in red).

Summary

Raman microscopy is a very powerful method for analyzing the complex multi-layer structures that are used in disposable diapers and other sanitary products. This technique allows identifying the various layer and fiber materials that form the diaper. Even individual substances like fillers and additives can be determined. Based on the obtained chemical contrast it is possible to visualize the distribution of these materials down to the low micrometer range in chemical images. These images allow to determine the dimensions of structures like individual layers in a laminate, independent from their visual contrast and without the need to prepare microtome sections.

With the SENTERRA II Bruker offers a Raman microscope that allows to apply this analytical technique in a very comfortable manner. Due to a clearly structured, software-guided workflow and the fully automated hardware the SENTERRA II provides the level of efficiency that is needed in industrial R & D and failure analysis.

Bruker Scientific LLC

Billerica, MA · USA
Phone +1 (978) 439-9899
info.bopt.us@bruker.com

Bruker Optics GmbH & Co. KG

Ettlingen · Germany
Phone +49 (7243) 504-2000
info.bopt.de@bruker.com

Bruker Shanghai Ltd.

Shanghai · China
Tel.: +86 21 51720-890
info.bopt.cn@bruker.com

www.bruker.com/optics