Fast identification of low molecular contents (additives) in tailor-made polymers with FTIR-coupling

P. Montag, M. Adler; PSS Polymer Standards Service GmbH; POB 3368, D-55023 Mainz, www.polymer.de; e-mail:PMontag@polymer.de

Introduction

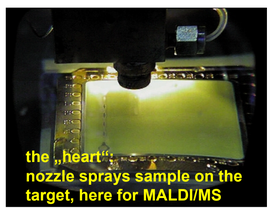
Modern polymer materials are very complex mixtures. Beneath the molecular polymer structure (copolymers, chain-branching, blends) various additives (antioxidants, slipping agents and more) can be found. For both cases a good analytical tool to identify and quantify is recommended. The hyphenated technique of GPC-FTIR coupling is a fast and stable method. Time intensive extractions or fractionations have been reduced or eliminated.

In some cases, identification of additives and polymers can be done in one single GPC-FTIR experiment. In other cases a short time (1 day) extraction with LC-FTIR coupling gives good FTIR spectra, by which additives can easily be identified in a library search. The LC-FTIR-coupling technique can be added to existing FTIR-spectrometer and LC-components.

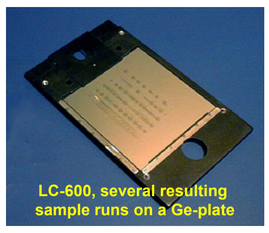
Following examples show results from typical samples of this coupling technique.

Technique

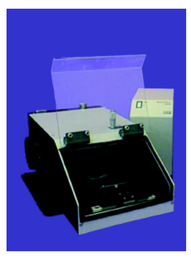
The online collection module
In the first step a LC interface (LC-600) is added to the waste-line of the liquid chromatography system. This PC driven interface fractionates the samples and evaporates the solvent in one online step. The mixture is separated on a target (Ge-plate or MALDI) and can be analyzed in the second (offline) step by spectroscopic methods.

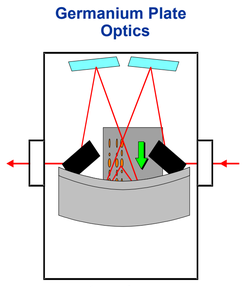


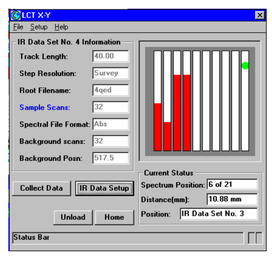
The nozzle
The „heart“ of this technique is the nozzle:
A preheated gas stream (N_2, dry air) is mixed with the solvent/sample. When the spray leaves the nozzle, the solvent evaporates and the sample is deposited on the target.



The spectroscopic analysis:
In this offline step the target is transferred to a spectrometer. For additive analysis FTIR together with a library search is a powerful tool. The sample trace on the germanium-plate can be scanned automatically with a x,y-optics module. This is PC-controlled and works together with most commercial FTIR spectrometers and software. Up to 10 chromatograms with any number of scans/spectra can be collected automatically. The result is a series of solvent and interference free FTIR-spectra.







Summary

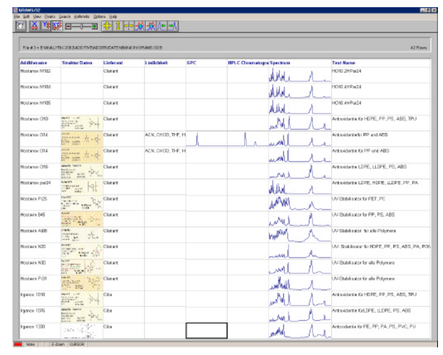
LC-FTIR is an easy to use, non-destructive method for analyzing additives. Combining the chromatograms of GPC and HPLC together with FTIR-spectra (e.g. in Grams 32) creates an effective database with 3 independent parameters. Other results (MS) can be added too. Once separated and applied to a Ge-plate, the additives may be analyzed not only by FTIR, but by other methods like MS, NMR or UV as well.

In summary, LC-FTIR is a powerful tool to establish methods for additive analysis with new possibilities in identification and quantification.

Adding the results of Coupling to a database (created with Grams 32 software):

- **Adding Chromatograms from GPC and/or HPLC to a database**
- **Adding resulting FTIR-spectra**

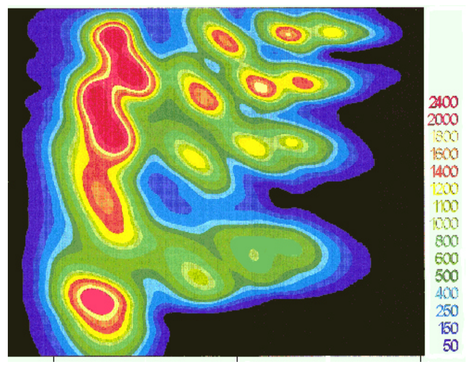
☞ **creates a database of Additives with possibility to search 3 different types of information (GPC, HPLC, FTIR)**



Outlook

Additive enrichment methods for higher sensivity and fast separation methods are the main fields of future investigations. Combination of new HPLC and GPC methods (as shown for 2D chromatography in the picture) with FTIR, especially for polyolefins, will be our future work:

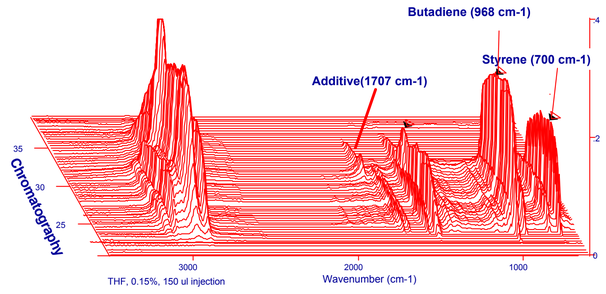
The aim is to change from time-intensive extractions to fast automated LC-separations for all kinds of polymers.



Results

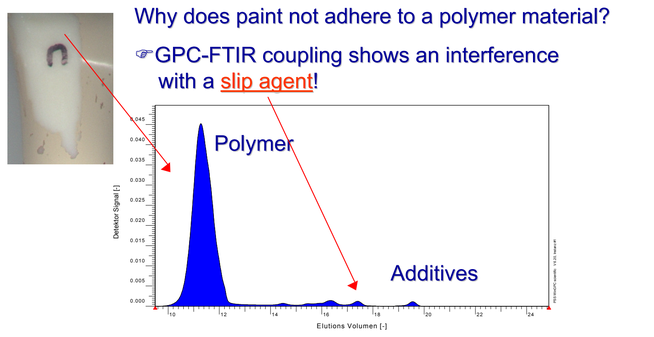
1. example: direct additive analysis with GPC-FTIR in a copolymer

First example shows a styrene-butadiene copolymer, that was coupled directly with a typical THF-GPC run. The main interest here was the copolymer content. When it contains an additive and the concentration is high enough, it can be directly identified in the resulting spectra. In the 3-d plot of this sample the additive is easily found because of its C=O-bonding.



2. example: direct GPC-FTIR coupling for trouble shooting

This second example shows a typical analytical question. A lacquer could not be fixed accurately on a polymer surface. The GPC analysis of good/bad samples showed, that the polymer was identical, but in the low molecular separation region one peak was more intensive for the „bad case“. A direct FTIR coupling gave the solution for the problem: a slip agent was not removed from the surface in the „bad case“.



GPC: THF, 1 ml/min SDV 10000/1000/100A, RI Detector

3. example: GPC-FTIR coupling after extraction

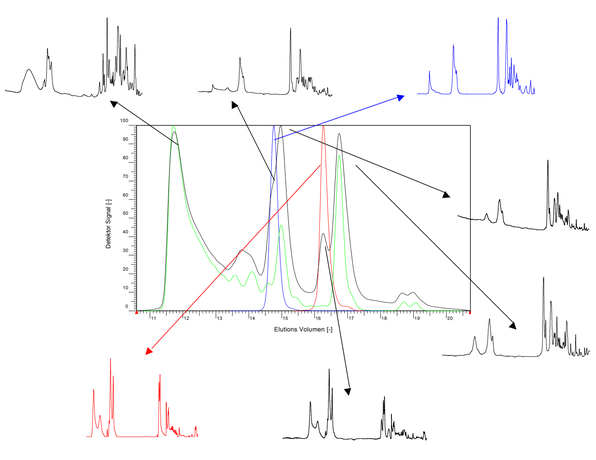
Because of several reasons (low concentration, insoluble polymer, i.e. PP or PE) sometimes a direct GPC-FTIR coupling is impossible or inaccurate.

An optimized pre-treatment of the sample can extract all low molecular contents in a complex polymer mixture. Procedures for pre-treatment include pulverization of the samples, extraction with dichloromethane and a possible ultrasonication.

The method most used for the analysis of those extracts is GC/MS. A drawback, especially when using head space techniques, is that some additives are decomposed. Quantification can be a second problem.

Using a LC method with the nondestructive FTIR is an easy to use alternative. The given example shows an extract of a polymer mixture containing an antioxidant and a slip agent.

This „simulated“ polymer (additives were added into the polymer, it is not a technical product) shows, that it is not necessary to get a baseline separation of each peak. The resulting spectra are „pure“ enough to identify the additives using a library search.

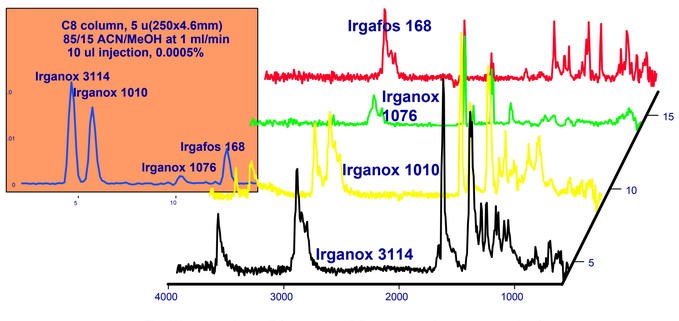


THF-GPC: 1 ml/min, PSS Oligomer-GPC columns

black: mixture in GPC with resulting FTIR spectra
green: polymer in GPC with resulting FTIR spectra
blue: antioxidants in GPC with resulting FTIR spectra
red: slip agent in GPC with resulting FTIR spectra

4. example: HPLC-FTIR coupling after extraction

HPLC is a very common method for the separation of additives. There exists a variety of different applications for additive separation. Because of the independence from separation mechanisms, FTIR can be coupled with HPLC as well as with GPC. After extraction of the additives from a polymer, a HPLC separation with identification via FTIR is possible. This example shows the sensitivity of the coupling technique. A mixture of 4 different additives (50 ng each) was injected into a typical HPLC system. All additives could be identified easily by means of a library search. The given figure shows possible problems: because of different FTIR-sensitivities the same concentrations show different signal intensities, so a quantification requires a calibration for each compound. The HPLC separates according to the interaction of a compound with the stationary and the mobile phase. If the interaction with the stationary phase is too strong, the material will not elute completely. A way to circumvent this, is to choose a GPC separation. In GPC the separation will be performed corresponding to the molar mass of the analytes. So the method and possible adsorption need not be verified prior to analysis, because all low molecular compounds elute in the same region of the chromatogram.



Each sample = *50* ng 32 scans, 4 cm^{-1} resolution

5994-6800EN
DE15891359