BULLETIN: DEFORMULATION OF PACKAGING

1. INTRODUCTION

Today there are various methods for the analysis of materials in their various phases (solid, gaseous and liquid). The success of the characterization depends on the isolation of the individual components and a suitable selection of tools for the investigation. Typical material properties and analysis methods can be seen in Table 1.[1]

No research can be done without the right materials and tools. Thus, for example, polymers and pigments require corresponding instrumentation for identification and characterization via infrared spectroscopy and X-ray diffraction. It is rarely necessary to use all of the techniques listed in Table 1 to identify the components in a formulation, but the use of more than one method is recommended to obtain reliable results. Always is recommended the use of a standard or control sample to compare with the sample being studied. [1]

Packaging materials are usually made up of several layers that fulfill different functions. Polymers are mainly used as a laminating material, but other materials such as aluminum are also used. Also other layers can be added for adhesive sealing or printing.

Defects in multilayer systems can affect product performance. Since many of the different materials that make up the structure cannot be distinguished visually and the defects are often microscopic, selective analysis of these defects is often difficult. [2]

Table 1. Material properties and analysis methods[1]

Properties	Analysis methods	Acronyms	Magnitudes	Acronyms
Colo	Optical microscope	OM	surface/mass	(S/M)
Virtual image and	Optical microscope	OM	Surface	(S)
S	Optical microscope	OM	Surface	(S)
Elemental Identification	Energy dispersive X-ray spectroscopy	EDXRA	Surface/Mass	(S/M)
Chemical Identification	Electron Probe Microanalysis (EPM), Auger Electron Spectroscopy (AES), Electron Scanning Chemical Analysis (ESCA), Infrared Spectroscopy (IR), Atomic Spectroscopy (AS), X-Ray Diffraction Spectroscopy (XRD), Raman Spectroscopy (ER), Nuclear Magnetic Resonance (NMR), Gas Chromatography (GC), High Performance Liquid Chromatography (HPLC)	EPM, AES, ESCA, IR, AS, XRD, ER, RMN, GC, HPLC	Surface/Mass	(S), (S), (S), (S/M), (M), (M), (M), (M), (M), (M),
Crystal form and degree of	X-ray diffraction (XRD) spectroscopy, Ultraviolet (UV) spectroscopy	XRD, UV	M	(M)
Melting Temperature	Differential Scanning Calorimetry (DSC), Differential Thermal Analysis (DTA)	DSC, DTA	M	(M)
Glass transition	Differential Scanning Calorimetry (DSC)	DSC	M	(M)
Decompositio n	Thermogravimetric analysis (TGA)	TGA	M	(M)
Molecular weight of polymers/resins	Size exclusion chromatography (GPC)	GPC	M	(M)

Multilayer polymeric films are used in a variety of industries and are manufactured using coextrusion and lamination techniques. Strict control of the quality and composition of these films is important to both manufacturers and the industries that use them. [3]

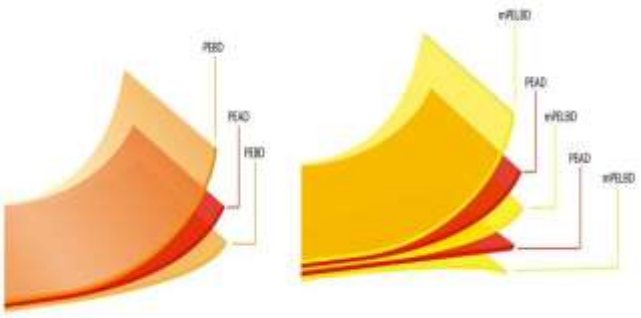

Figure 1. Multilayer film.

2. DEFORMULATION

Deformulation refers to a set of analytical procedures used to separate and identify individual components of a formulated chemical. [4] [5] [6] This technique applies methods from analytical chemistry and is often used to obtain competitive intelligence[1] about chemicals.

The deformulation technique is related to reverse engineering; [7] [8] however, the latter concept is more closely associated with the procedures used to discover working principles of a designed device or system by examining and disassembling its structure.

The deformulation of a multicomponent chemical mixture can occur in various contexts, including the investigation of the causes of the failure of the chemical product, competitive benchmarking2, legal investigation to obtain evidence of patent infringement, or research and development of new products; Depending on this context and the level of information sought, the analysis requirements for deformulation may be different. [9]

Deformulation processes typically require the application of several analytical methods, and the selection of methods depends on the required degree of confidence in the results.

Figure 2. Deformulation to formulate.

3. GENERAL DEFORMULATION TECHNIQUES

The deformulation of compounds follows a protocol, which depends on the type of material to be deformulated, such as the scheme shown in Figure 3. Various techniques to identify the components of a compound are described below.

[1] The **deformulation of compounds** follows a protocol, which depends on the type of material to be deformulated, such as the scheme shown in Figure 3. Various techniques to identify the components of a compound are described below.

[2] According to David T. Kearns, CEO of Xerox Corporation **"benchmarking** is a systematic and continuous process to evaluate the products, services and work processes of organizations recognized as best practices, those toughest competitors".

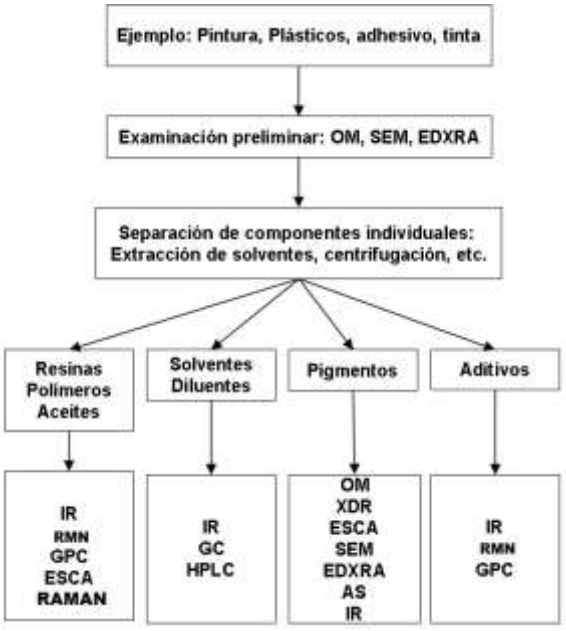

Figure 3. Basic scheme of deformulation for paints, plastics, adhesives and inks. [1]

3.1 Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) is a powerful thermal analytical tool that performs quantitative calorimetric measurements on solid, liquid or semi-solid samples. The DSC measures the amount of heat that flows into or out of the sample using temperature sensors that are positioned in the heating block of a "heat flux" DSC.. [10]

In this technique, a temperature program is applied to a sample and an inert reference material in the DSC cell, and sensors measure the temperature difference between them. When the sample undergoes a thermal process that produces heat, such as crystallization, the resulting test plot or thermogram shows an increase in heat flow. This is indicative of an exothermic event because the temperature recorded by the sample sensor is higher than that detected for the reference. If the sample undergoes a thermal event that causes it to absorb more heat than the reference (for example, melting), the thermogram shows an decreased heat flux. This is called an endothermic process and in this case the temperature sensor measures a lower temperature for the sample compared to the reference. [10]

Figure 4. DSC equipment available at INDESCA.

A typical scan via DSC involves heating the sample at a controlled constant rate, such as 10°C per minute, and monitoring the heat flux to characterize phase transitions and/or curing reactions as a function of temperature rise. The studies involved use multiple heating and/or cooling ramps as well as isothermal holding segments. [10]

Ideal Uses

- Characterization of relevant phase transitions (eg, melting, crystallization, glass transition, Tg), which can be used to determine the best processing temperatures and maxi
- Quality comparison (QC, failure analysis, evaluation of new materials) mum use temperatures.
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- Identification of unknown materials and determination of the presence of impurities.
- Evaluation of formulations, mixtures and effects of additives.
- Estimation of the percentage of crystallinity.

- Determination of percent purity of relatively pure organic compounds.
- Determination of phase separation of polymer and copolymer blends.
- Evaluation of the eutectic point, that is, the melting point of a mixture, being lower than that corresponding to each of the compounds in its pure state.

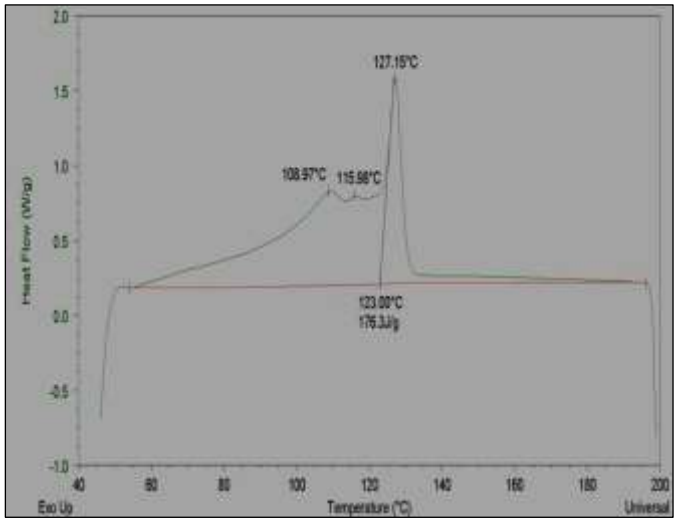

Figure 5. Composite film thermogram of LDPE, LLDPE and HDPE. (Source: Indesca, 2016).

- Characterization of polymorphic materials.
- Evaluation of the thermal history of compounds.
- Making sensitive measurements of subtle, weak, or overlapping phase transitions. (10)

Strengths

- Small sample size.
- Highly accurate and sensitive measurement of subtle or weak phase transitions and thermal capacities.
- Very precise temperature control.
- Possibility of separating superimposed thermal transitions (modulated DSC option) (10)

3.2 Thermogravimetric analysis (TGA)

Thermogravimetric or Thermal Analysis (TGA or TG) measures changes in sample weight in a controlled thermal environment based on of temperature or time. Changes in sample weight (mass) can be the result of alterations in chemical or physical properties and can be detected to a fraction of a microgram.

TGA is useful for investigating the thermal stability of solid or liquid materials under temperature gradient conditions in an inert or oxidative gas atmosphere; can also be carried out at constant temperature to assess the thermal stability of materials over a specific period of time.(10)

The coupling of TGA to a spectrophotometer allows the study of volatile species and pyrolysis products, which can lead to discovering how a compound or formulation degrades and what components it contains. For example, with the combination of a TGA coupled with a mass spectrometer (MS) specific information on the chemical structure can be obtained to identify additives, contaminants and the composition of mixtures and copolymers (TGA-EGA). (10)

Figure 6. TGA equipment available at INDESCA.

Ideal Uses

- Thermal stability / degradation.
- Volatile / Moisture Quantification.
- Additive screening.
- Evolved Gas Analysis (TGA with MS or TGA with FTIR).
- Vaporization or sublimation.

- Deformulation of organic / inorganic mixtures (eg ink, paste, polymeric compounds).
- Residue content / filling.
- Decomposition kinetics.[10]

Strengths

- Small sample size.
- Solid and liquid analysis with minimal sample preparation.
- Qualitative or quantitative analysis.
- Detection of multiple mass loss thermal events from physical and chemical changes of materials.
- Separation of overload thermal events from loss of mass (TGA of high resolution). [10]

3.3 Spectroscopy

3.3.1 Infrared Spectroscopy/Fourier transform (FT-IR)

FT-IR microscopy is an attractive method for failure analysis. It allows to measure an IR spectrum of structures in the micrometer range at high lateral resolution. IR spectra provide information on the chemical identity of the defects and allow different layers to be distinguished. With FT-IR microscopy, a chemical image of the sample can be recorded showing its composition and defect distribution. [2]

Fourier Transform Infrared Spectroscopy (FT-IR) is an effective analytical technique for rapidly identifying the "chemical family" of a substance. Typically, organic and polymeric compounds (and to a lesser degree, inorganic compounds) produce a "fingerprint" IR spectrum, which can be compared to the existing extensive reference database and the actual chemical family or identity of the unknown component. [10]

FT-IR measures the absorbance of infrared light by a sample and generates a spectrum based on the functional groups the material has. In addition to typical sample preparation methods (such as micro-extraction, dilution, pellets in KBr and grinding techniques), the FT-IR also uses various attenuated total reflectance (ATR) accessories, which allow direct examination of insoluble or multilayered samples. [10]

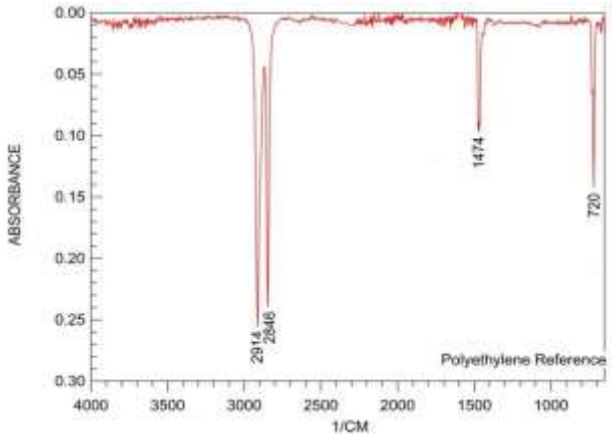

Figure 7. FT-IR Reference Spectrum of Polyethylene.[11]

Ideal Uses

- Characterization and identification of complex mixtures, including gases, liquids and solids.
- Identification of organic contaminant (eg particulates, debris) at the macro and micro scales.
- Oxygen and hydrogen quantification. [10]

Strengths

- Ability to identify organic functional groups and often specific organic compounds.
- Extensive spectral libraries for compound and mixture identification.
- Ambient conditions (vacuum is not necessary, and is applicable for semi-volatile compounds).
- Minimum scan area (limit of detection): ~ 15µm. Inch ruler: if the sample is visible to the human eye, it is likely that it can be analyzed.
- Can be quantitative with appropriate standards and uniform sample thicknesses.
- Complementary to Raman spectroscopy. [10]

3.3.2 Resonance Spectroscopy nuclear magnetic (NMR)

Magnetic Resonance Spectroscopy Nuclear (NMR) is a powerful analytical technique that can reveal structural information about many organic and inorganic molecules. In NMR, the magnetic nuclei of specific isotopes are aligned by a strong external magnet and then perturbed by a radio wave. This external energy applied to the molecule is absorbed and the perturbed nucleus is said to be "in resonance". The resonance frequency is observed as re-emitted energy, and is related to the identity, quantity, position, and intramolecular relationships occurring within the analyzed substance [(10)]

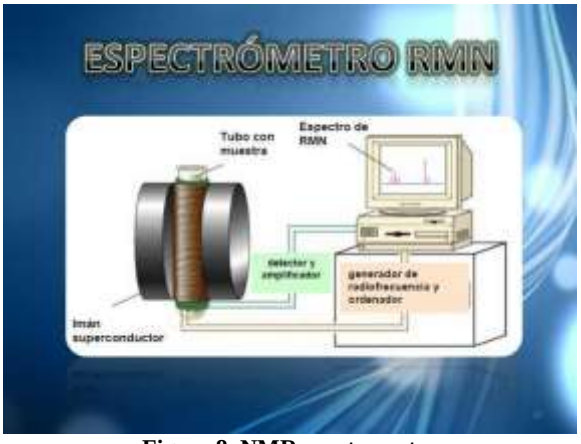

Figure 8. NMR spectrometer.

NMR is used to characterize polymers, lubricants, adhesives, surfactants, additives, and synthesized molecules. Samples are normally prepared in various deuterated solvents. Typical analysis times range from minutes to hours, depending on nuclei studied and sample concentration. [(10)]

Ideal Uses

- Identification of the chemical structure.
- Identificación y confirmación del compuesto.
- Análisis cuantitativo.
- Chemical composition analysis.
- Fingerprints of raw materials.
- Determination of sample purity.
- Identification and confirmation of the compound.
- Quantitative analysis.
- Polymer end group analysis.[(10)]

Strengths

- Chemical changes and couplings in J or Scalar (dipole-dipole coupling indirect) can provide information specific chemistry.Analysis of the chemical composition.
- Quantitative information.
- You can provide information about composition with mixtures.
- Non-destructive method.
- Requires few samples
- Wide range of temperature operation. [(10)]

3.3.3 Raman spectroscopy

Raman microscopy is an excellent means to achieve identification of different polymeric materials. The technique is highly sensitive to small changes in molecular structure and branched configurations and is therefore ideal for polymer identification. Raman microscopy requires almost no sample preparation. [(3)]

Confocal analysis[3] generates rapid depth profiles with 2 µm spatial resolution, while cross-sectional analysis of multilayer films provides 1 µm or better resolution. Spectral differences can be exploited to estimate the thickness of constituent layers, while spectral search libraries identify their composition. Likewise, the confocal analysis and the high spatial resolution of Raman microscopy also make this technique ideal for identifying the source and identity of defects and inclusions in polymeric films. [(3)]

[3] Confocal microscopy is a technique that eliminates out-of-focus light in specimens and enables 3D imaging of thick specime
.

Raman Spectroscopy (Raman Analysis) allows chemical structure determination and compound identification using vibrational spectroscopy. Raman has better spatial resolution than FTIR and allows analysis of smaller dimensions, down to the 1 µm range. [10]

Figur6 9. Raman spectrómeter available at INDESCA

Raman is an ideal technique for the qualitative analysis of mixed organic and/or inorganic materials and can also be used for semi-quantitative and quantitative analysis.

Ideal Uses

- Identification of the molecular structure of organic and inorganic compounds for contamination analysis and classification of materials.
- Identification of materials in multilayer polymeric structures.
- Determine inorganic oxides and their valence state.
- Determine the presence of different types carbon (diamond, graphite, amorphous carbon, diamond-like carbon, nanotubes, etc.) and their relative proportion.
- Characterization of carbon layers (graphitic diamond vs. orientation and structure random versus organized structure).[10]

Strengths

- Ability to identify organic functional groups and often specific organic compounds.
- Spectral Libraries for Compound Identification.
- Ambient conditions (does not need high vacuum, therefore good for semi-volatile compounds).

4. Case studies of the applicability of deformulation in industry

Below are three case studies that illustrate the applicability of deformulation in industry:

Case 1

A manufacturer of multilayer films for the food packaging industry needed to measure the thickness of each of the layers to comply with its quality control protocol. Likewise, it needed to identify the composition of the layers used to build the products of the competition.

Solution: A combination of polarized light microscopy and infrared microscopy was used to photograph, measure and identify the separate layers of the film in cross section.[13]

Case 2

Una empresa fabricante de reguladores de voltajes y pantalla plástica para bombilla LED, solicitó la caracterización de los productos: resina polimérica en gránulos, color negro y pantalla plástica transparente; ambos productos tomados de la exhibición de una feria internacional.

Solution: Polymeric matrix identification assays were performed via differential scanning calorimetry (DSC) and infrared spectroscopy, FTIR/ATR. Both techniques allowed to identify the materials used for the fabrication of the samples.[14]

Case 3

A company that produces chicken sausages required the development of packaging for this application, to replace their importation with nationally produced packaging.

Solution: the polymeric matrix of the reference sample was determined via differential scanning calorimetry (DSC). This technique was complemented with tests of mechanical, sealing and gas permeability properties, which allowed recommending the composition of a multilayer structure for the manufacture of packaging. [15]

Figure 10. Multilayer containers.

RESUME

Multilayer polymer structures are used in a variety of industries. In food packaging, for example, polymeric laminates are used not only to protect foods, but also to retain aromas and flavors, and to extend shelf life.

Multilayer films are produced using coextrusion and lamination techniques. Some of the problems that can occur during film manufacturing include the introduction of defective particles and separation of the layers. Current analytical methods that examine materials during and after production include NMR and DSC. [3]

Vibrational spectroscopy is a valuable addition to these techniques as it provides definitive molecular information. Raman spectroscopy is complementary to FT-IR spectroscopy and offers benefits including higher spatial resolution and easier sample preparation. [3]

Dispersive Raman spectroscopy uses visible lasers (400-785nm) for sample excitation. Compared to FT-Raman, the use of visible lasers allows for higher spatial resolution (better than one micron), and since the Raman emission is proportional to $1/\lambda$, the sensitivity is much higher. [3]

Raman spectroscopy is sensitive to both chemical and physical properties, and its unique selection rules generate a molecular fingerprint that is suitable for material identification. The technique is particularly sensitive to molecular structure and branched structures. This makes it ideal for polymer identification and defect analysis. [3]

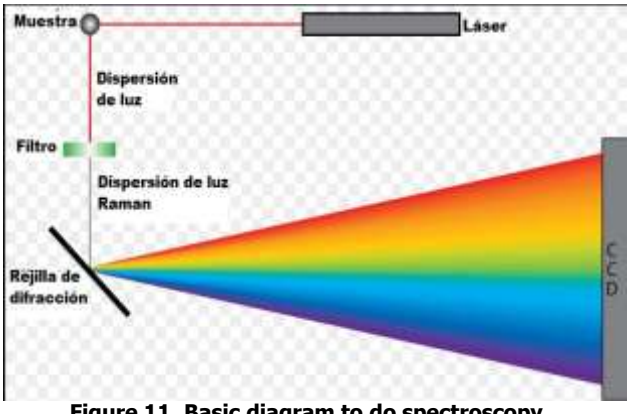

Figure 11. Basic diagram to do spectroscopy Raman. (Source: www.researchgate.net). [8]

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