METHODOLOGY FOR FINGERPRINTING OF MATERIALS AND PROCESSES

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ABSTRACT

This paper presents the different approaches and analytical methodologies developed in the frame of this study for gaining advanced knowledge on the composition of specific classes of materials used in aerospace industry. The results will allow the partners to anticipate potential obsolescence with rational proposals for alternative materials.

ABBREVIATIONS

BPA: Bisphenol A
DGEBA: Diglycidyl ether of bisphenol A
DMA: Dynamic Mechanical Analysis
DSC: Differential Scanning Calorimetry
FTIR: Fourier-transform infrared spectroscopy
GC: Gas chromatography
HPLC: High-performance liquid chromatography
NMR: Nuclear magnetic resonance
SEC: Size-exclusion chromatography

INTRODUCTION

To face the risk of obsolescence that may impact critical and strategic materials for aerospace and defense industry, there is a need for gaining a deeper knowledge and understanding on the composition-performance relationship in a variety of formulated products. These products generally include a limited number of main components together with several additives and likely high concern trace contaminants. The aim of this project is to perform detailed characterization of the physical properties and technological performances of critical products and materials as a function of their composition in key components, in order to minimize risk in program management and to reduce development and qualification costs for alternatives.
The change to new materials is directly or indirectly, to environmental regulations, market disruptions or economical strategies with a dramatic industrial impact (caused reliability, planning, economic...) due to the need of re-qualifications.

The deep knowledge of materials composition and performances will allow space industries to be proactive in case of materials obsolescence, minimizing risk, cost and time to define precisely the necessary tests to be performed depending on the nature of changes made in composition.
From a material perspective, the study was focused on a limited number (20) of strategic and critical materials used commonly in space industry that could be impacted (directly or indirectly) by European or country legislation and then become obsolete.

In order to anticipate the obsolescence of specific formulation compounds this study aims at:

- obtaining the spectroscopic and analytical "fingerprints" of various classes of complex compositions (paints, adhesives, varnishes, lubricants, films …),
- identifying their risk with respect to obsolescence,
- deformulating representative materials with different degrees of refinement,
- comparing their composition and properties (old/new formulations),
- suggesting orientations for new and sustainable formulations and materials.

STUDIED MATERIALS

The selection of the different materials was performed in order to cover the widest range of applications identified for space application, including structural or multi-purpose adhesives, compounds with optical or electrical properties, primers, lubricants, varnish and paint.
The proposed compositions are, for the most part, mixtures of various constituents different in nature, physical form and chemical composition (typically different polymers, pre-polymers, fillers, pigments and additives). Some materials are in the form of films or adhesive tapes.

This paper will present an extract of some results obtained in the frame of the study in order to illustrate the applied methodology.

GLOBAL APPROACH AND METHODOLOGY

The analytical approach for gaining significant information on the composition of complex blends usually consists in the isolation of each component followed by structural characterization and quantification of the ingredients. This type of approach requires time, precise fractionation methods and advanced analytical tools (spectrometers, chromatography equipment…) to reach the target resolution of 0.1 weight-% for trace components or residues of high concern.

Rationale of the analytical approach

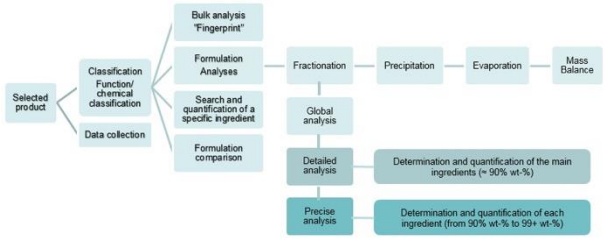

Fig. 1. Breakdown structure of the analytical approach.

The general approach that was followed can be summarized as a sequence of steps, as follows:

1. Analysis of literature and of technical data from suppliers;
2. Fingerprinting by spectroscopic methods (IR, NMR) and relevant chromatography techniques (HPLC, SEC, GC);
3. Rough determination and quantification of the main products;
4. Procurement and analysis of model compounds likely to be present (commercially available known components of a material);
5. Refined determination of product composition (loop back to step iv and v);
6. Depending on needs, qualitative and / or quantitative analysis of minor components (detection of specific component of interest, attempt to quantity the concentration of a substance of concern).

This global strategy has been tested and evaluated by implementing the sequence of steps detailed above essentially on three families of products, namely epoxy adhesives, polyurethane varnish and silicone elastomers.

RESULTS

1.1. Chemical Analysis

We illustrate in this paper our analytic approach by showing that the selected products can be analysed with various degrees of refinement, depending on the needs for global or for specific information. Fingerprinting by spectroscopic and chromatographic methods were implemented first to get global information on bulk materials, without or with limited isolation step. A second level consists in the determination of the class and rough quantification of the main ingredients in the formulations. This will allow for comparing two grades of epoxy adhesives commercialized under the same reference, before and after a slight change in composition disclosed by the supplier. Then we demonstrate that precise analyses aiming at the determination and at the quantification of minor components of concern can be performed.

Level 1 – Spectroscopic fingerprinting of the hardener of a two-component polyurethane varnish.

FTIR analysis provides a rough fingerprint of the polyol used as the hardener of the polyurethane coating material. However, variations of the relative intensity of the main bands assigned to the functional groups or of the squeleton of the hardener can be detected by a simple control analysis.

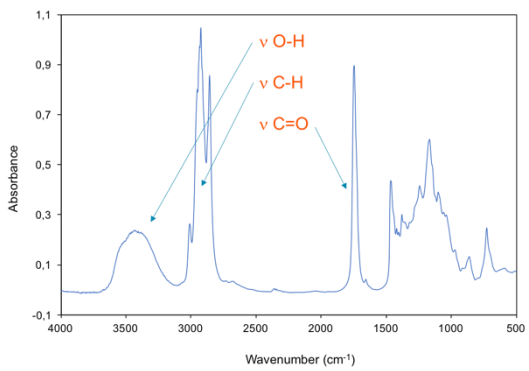

Fig. 2. FTIR transmission spectrum of the hardener for a 2-component polyurethane varnish.

^{1}H and ^{13}C NMR are much more informative, allowing for monitoring of possible evolutions in composition for a bio-based reagent, as a function of the production batch.

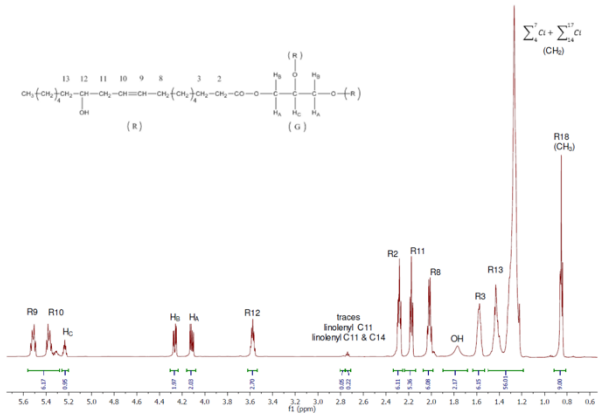

Fig. 3. ^{1}H NMR spectrum of the hardener for a 2-component polyurethane varnish.

The spectrum in Fig. 3, 4 confirms the nature of the polyol, a castor-oil based triglyceride. The good sensitivity and the resolution of the 600 MHz spectrometer reveals the presence of other fatty acids as minor constituents identified as linoleyl and linolenyl esters. The hydroxyl functional ricinoleate was estimated to represent 90 mol-% of the esters linked to the glyceryl moiety.

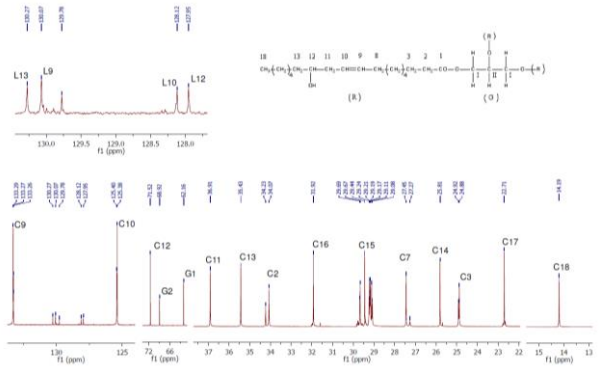

Fig. 4. ^{13}C NMR spectrum of the hardener for a 2-component polyurethane varnish confirming the nature of the polyol, a castor-oil based triglyceride, with other fatty acids components, besides the ricinoleic ester.

Level 2 – Changes in composition and upgrading of formulated products

A more advanced level consists in exploiting more quantitatively the main components of a complex blend. We have applied this approach for comparing the old and updated formulation of a base component of an epoxy adhesive.

The superimposed ^{1}H NMR spectra in Fig. 5 do not reveal significant changes in composition in the epoxy resin. However, minor changes in very small signals corresponding to silane coupling agents were detected upon careful examination of the expanded spectra.

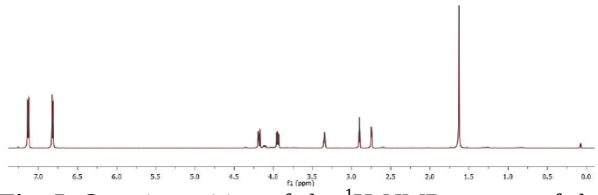

Fig. 5. Superimposition of the ^{1}H NMR spectra of the "old" (red line) and of the "new" (blue line) grade of the epoxy-based adhesive supplied under the same reference.

HPLC analyses were performed on the same "old" and "new" formulations, to gain complementary information on the composition in the various oligomers of the DGEBA epoxy resin.

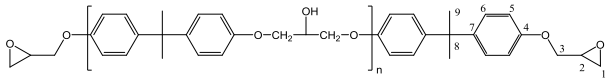

Fig. 6. Simplified representation of the structure of the oligomers(n= 0, 1, 2, …) in DGEBA-based epoxy resin.

Typical chromatograms obtained by HPLC analysis of both grades of the epoxy resin are reproduced in Fig. x. The oligomers with n = 1 and 2 are detected as minor constituents. The precise content can be deduced from the respective area of the different peaks after appropriate calibration.

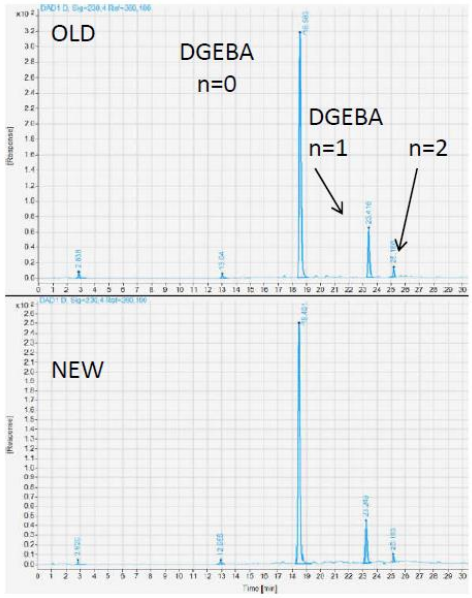

Fig. 7. Comparison of the replicated chromatograms of the "old" and of the "new" grade of the epoxy-based adhesive supplied under the same reference.

The 2 chromatograms appear very similar, suggesting that the compositions are quite identical. This was confirmed by replicating 5 times the analyses. However, the standard deviation for the analyses conducted with the "new" grade sample was much higher than with the "old" one (Table 1).

Tab. 1. Retention times (Rt) and fractional area (%-area) of the peaks observed for the various oligomers of DGEBA in the chromatograms of Fig. 7.

	Old (5 samples)		New (5 samples)	
Rt (min)	% area	σ	% area	σ
18.54	84.0	0.1	85.5	0.8
23.38	14.0	0.05	12.9	0.6
25.15	2.0	0.1	1.8	0.2

These unexpected results might originate from some fluctuation of composition in the newer batch, possibly because of insufficient mixing prior to conditioning.

Additional experiments were also conducted to detect trace amounts of aromatic solvents in the formulations.

Level 3 - Quantification of specific components

Epoxy resins based on diglycidylether of bis-phenol A (DGEBA) are generally mixtures of various oligomers and isomers (glycidyl groups located in para, para – p,p'; ortho, para – o,p'; ortho, ortho – o,o' positions). The resins also include unreacted starting compounds and by-products. For controlling the possible presence of chemicals of concern, various epoxies and their precursors were characterized by ^{1}H / ^{13}C NMR and by HPLC as model compounds.
A calibration curve was then made to determine the bis-phenol A (BPA) detection limit in solution at λ = 230 nm. Solutions including BPA at various concentrations, with or without DGEBA were analyzed by HPLC to establish a calibration curve.

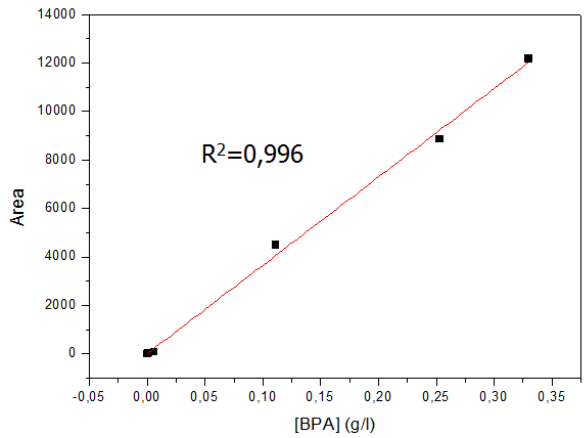

Fig. 8. Calibration curve based on the dependence of area of the peak assigned to BPA in HPLC chromatograms with detection at 230 nm.

The detection limit for bis phenol-A (BPA) in solution was assessed at about 0.18 ppm with respect to the mass of the analyzed solution. This technique can be used to assess the amount of BPA either in the uncured resin or in the solution obtained from a cured sample submitted to Soxhlet extraction.

A representative sample of cured epoxy adhesive has been prepared and submitted to Soxhlet extraction in acetonitrile. The extracts analysed by HPLC in the same conditions as for the calibration experiments reveal the the presence of various isomers and oligomers together with a noticeable amount of BPA (Fig. 9).

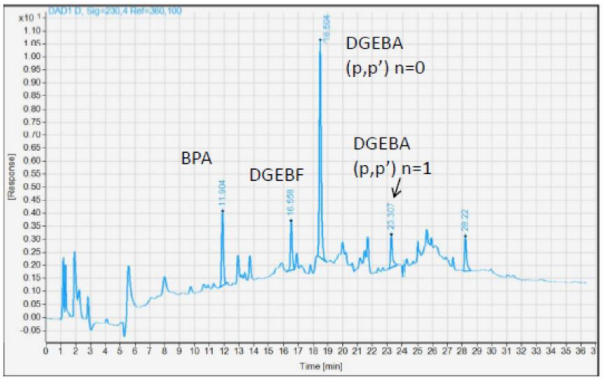

Fig. 9. HPLC chromatogram of the Soxhlet extracts from a cured epoxy-amine adhesive revealing the presence of various isomers and oligomers together with a noticeable amount of BPA.

1.2. Physical Analysis

The physical analysis was performed on the polymerized materials, once processed. Among the different techniques considered and depending of functional properties of interest of the materials the following ones have been implemented:

- DSC,
- DMA,
- Shear strength test,
- Thermo-optical properties.

The aim of these characterizations is to identify and measure the key parameters of the material, related to their intrinsic properties (DSC, DMA) or associated to their final functional properties of interest (shear strength, adhesion, thermo-optical properties…).
These reference measurements will constitute a database allowing the assessment of the potential impact of the change in formulation and to status on their acceptability with regard to the final application.

Tab. 2. Lap-shear strength for old and new formulation of two epoxy adhesives.

Material	Mean Failure Load (MPa)		Failure Type
	Old	*New*	
E1/2	32.7	30.8	Mixed
E4/5	20.3	21.1	Mixed

To illustrate this approach, the results obtained during lap-shear strength test on two epoxy adhesives that have undergone a change in formulation are displayed above (Tab. 2).

CONCLUSION

In the frame of this study, a panel of materials widely used in space industry has been considered and analysed. A global strategy and a specific methodology have been defined, validated and implemented in order to perform deep analysis of the materials. The results obtained in the frame of this study will allow for building of a database with reference values that will help to assess potential criticality in case of formulation change of one of these materials.

ACKNOWLEDGEMENTS

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