UNIVERSITÀ DEGLI STUDI DI PADOVA

DIPARTIMENTO DI INGEGNERIA INDUSTRIALE

CORSO DI LAUREA MAGISTRALE IN INGEGNERIA CHIMICA E DEI PROCESSI INDUSTRIALI

Tesi di Laurea Magistrale in Ingegneria Chimica e dei Processi Industriali

Predicting key performance features of packaging tubes from the mechanical properties of the constituent material through multivariate statistical modelling

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ANNO ACCADEMICO 2021 – 2022

Abstract

The most recent developments in terms of material reduction have pushed towards ever so thin tube walls, to the point that the mechanical resilience of the tube can not be assumed or simply verified qualitatively, but needs measurement. Hence the need for a testing methodology to quantify tube mechanical performance.

The work presented in this study regards the development and validation of a cyclic mechanical test to quantify the tube resilience to different imposed deformations.

Moreover, a methodology for treating the test results is devised, in order to obtain a *denting curve*, uniquely characterizing the deformation behavior of the tube.

Furthermore, a statistical model is developed to predict denting curves from the mechanical properties of the constituent material. This proves particularly useful in all those instances in which it is desired to evaluate a new material for use in tube manufacturing without actually producing tube samples.

Ultimately, an index for the rapid quantification of tube mechanical performance is defined. The value of the index (*denting index*) is obtained from the analysis of the corresponding denting curve. The rapid assessment of a tube's mechanical performance becomes thus possible by simply predicting or measuring its denting index.

Contents

Introduction

In this work, the results of six months of internship at the Global Innovation Center of Procter & Gamble (P&G) in Schwalbach am Taunus (Germany) are presented.
On this Campus, students from all over the world take part in the effort to enhance the quality and the performance of P&G's products through the use of high-end technology and advanced modelling.
The activities were carried out with the collaboration of the Hair Care Packaging MPD team, specifically working on the development of methodologies for a quantitative evaluation of packaging tubes performance.

The packaging tube represents a considerable share within the world of plastic packaging thanks to its moderate cost, high printability, and peculiar barrier properties. It was first introduced in 1841 by John Goffe Rand [17], and since then it has been a viable option for containing and dispensing viscous fluids.

In recent times a shift in paradigm has involved the world of packaging: as the concerns about product sustainability and recyclability grow in popularity, the manufacturers of plastic packaging and their customers have become more and more interested in new solutions to respond to the needs of the market. For once, new packaging solutions should grant recyclability, thus abolishing or limiting inter-class composite materials, moreover, polymeric materials should be used to the least possible extent and with the highest possible content of recycled material.

These needs have pushed the ongoing proposal of innovative materials for tube manufacturing. All new materials are primarily developed to also grant adequate printability and the required barrier layer properties; such properties are easier to certify by performing measurements on sheets of the material; it is instead more difficult to quantify the mechanical resilience of a finished tube, and consequently, the adequacy of the packaging under such aspect has so far been assessed by means of the arbitrary judgment of the tube manufacturer and their customers. This approach was more than adequate in the past, given that the thickness of the tube wall was much greater than the bare minimum needed in terms of mechanical resistance.

As the tube wall gets thinner, it is not possible anymore to qualitatively evaluate or even just assume the adequacy of the mechanical performance of the finished tube. Measurements are needed, and thus a testing methodology has to be developed.

Thus, the focus of the project was initially to develop a method to quantitatively assess the impact of a change in material and wall thickness on the performance of packaging tubes.
The development of such a method is important to optimize and accelerate transitions to new materials and to avoid the uncertainty associated with subjective criteria (risk of discarding potentially good materials or vice versa).

The scope of the project was ultimately broadened, developing a model to predict the performance of tubes from the mechanical properties of the constituent material.
Such a model makes it possible to simulate the performance of materials for use in packaging tubes without the need for a finished tube, just requiring a sheet of the constituent material to run standard mechanical tests on.

In this regard, the model helps in operating a preliminary selection of the best-performing alternatives among a set of possible materials, without the expensive and time-consuming production of finished samples. Sample manufacturing and testing can then be performed on the best-performing materials (according to the predictions).

Study layout

The layout of the study is the following:

- the first chapter (State of the art) contains:
  - a brief presentation of the tube and its history;
  - a list of practical advantages and peculiarities of tubes;
  - a description of the tube manufacturing process;
  - an overview of existing methodologies and models for packaging performance evaluation and prediction.
- the second chapter (Materials, Instrumentation, and Methods) contains:
  - a list of tubes available for the study;
  - the necessary instruments, including testers and software;
  - a presentation of the employed standard mechanical testing methodologies;
  - a presentation of the mathematical methodologies employed for data pretreatment and modelling.
- in the third chapter (Results) all the achievements of the study are presented:
  - the development of a conceptual framework;

  - the definition and validation of a testing methodology to quantify the denting phenomenon;
  - the development of software for the automatic management of the raw data retrieved from the experiments;
  - the identification of a set of main variables involved in tube denting through the statistical design of experiments;
  - the development of a predictive model to evaluate the denting performance of a tube from the mechanical properties of the constituent material;
  - the proposal of a denting index to easily quantify denting performance, and of a diagram to compare denting indices of different tubes.

Implications of the study

In short, the outcome of the study consists of both a methodology and a model for a rapid and economical evaluation of the performance of new materials for use in tube production.
The capability to perform such evaluations represents a new tool in the hands of the Hair Care Packaging MPD team, rendering it easier to push forward a series of initiatives:

- **Cost savings**

  The screening of potentially interesting solutions becomes:

  - Quantitative: it is based on physical measurements with standardized procedures and equipment, it is thus repeatable, has a defined uncertainty range, and makes possible an objective comparison among materials.

    This eliminates the arbitrariness in tube selection, reducing the risk of poor choices.
  - Quick: only a sheet of the material is needed, without manufacturing the finished tube.

    This translates into faster and cheaper tests, also meaning that more options can be explored and testing materials originally developed for different purposes is now possible.

- **Material reduction**

  As discussed, the effort to reduce the thickness of different packaging solutions has been going on for years; such a task is not trivial, requiring profound mutation both in the materials and in the manufacturing processes, to guarantee the integrity of the item. This project is a step forward in such direction, leading once again to cost savings and aligning with the sustainability goals of the company.

- **Improvements in recyclability**

Developments in tube packaging often concern the adoption of completely new materials; this is especially the case when it comes to the substitution of inter-class composites, which used to be the solution of choice and are now considered obsolete because of their poor recyclability. In these cases, the choice of the material has to be completely rethought, and consequently, a testing methodology to evaluate the performance of new candidates proves useful.

Chapter 1

State of the art

1.1 The packaging tube

First and foremost, let's introduce the packaging tube through a broad definition: a packaging tube, squeeze tube, or collapsible tube is a cylindrical flexible package composed of three main parts:

- **tube body**: a cylindrical, hollow piece with a round or oval profile, made of plastic, paperboard, aluminum, other metals, or, as is often the case, a combination of such materials;
- **tube shoulder**: tapering section, in place to provide a nozzle (or more generally an orifice) for the dispensing of the product; can be formed from the tube body (aluminum tubes), or welded/formed in place (extruded/laminate tubes).
- **tube cap**: terminal part of the tube; it is fixed on the shoulder and seals the package, can be either screwed or steadily fixed with a flip-top function.

The end opposite the cap and shoulder is sealed by either welding or folding.

The purpose of tubes is mainly to allow precise dosage of viscous fluids, such as toothpaste, farmaceuticals, artist's paint, adhesive, and cosmetics. The tube's flexible nature proves ideal in aiding the dispensing of such fluids through hand pressure in all those applications where the more common bottle would prove inadequate. [1]

1.1.1 Packaging tube history

For the sake of completeness, a brief history of the packaging tube, which dates back to the XVII century, is reported:

"The tube was invented in the USA by John Rand, who applied for a patent in 1841. The first tubes to be produced in larger quantities were made from tin and were produced in France for use with paint. Later on, tubes made from lead were launched on the market.

The first machines for producing aluminum tubes were built in Germany in 1914. But it was not until the 1940s that aluminum tubes finally superseded those made from lead or tin.

Extruded tubes arrived on the market during the 1950s and the first tubes laminate with an aluminum barrier layer (ABL) appeared at the beginning of the 1960s. Laminate tubes with barrier layers made from plastic (PBL) and ceramic (CBL) then followed in the 1990s.

About 35 percent of all tubes produced in Europe today are made from aluminum, with about 25 percent attributable to plastic and about 40 percent to laminate tubes. Thanks to their special material properties, each of the tube types is used in specific fields of application and market segments. But when compared with other forms of packaging, they all offer those benefits that characterize the tube." [7]

1.1.2 Advantages of the packaging tube

Tubes represent a considerable share of the packaging market thanks to an incredible range of benefits:

- highest standards of hygiene, thanks to the inherent confinement of the content up to the moment of usage;
- excellent barrier properties;
- highly customizable mechanical properties;
- broad design opportunities;
- real consumer benefits in relation to the dispensing of viscous products;
- broad availability of environmentally sustainable designs.

Among all, one of the most interesting and peculiar advantages of the packaging tube is its notable barrier properties, which make it the solution of choice not only for viscous cosmetics products, but also for pastes in the alimentary and farmaceutical industries. It is in fact only thanks to such properties that the atmospheric oxygen can be kept out of the product and the volatile substance retained within the package.

In aluminum tubes the metal itself is responsible for hindering the diffusion of species; instead, in composite tubes the barrier properties are granted by elements within the layered structure of the tube wall (barrier layer), which are made of EVOH, biaxially oriented PP, aluminum, or ceramic coatings. Such a structure can be obtained through different processes, depending on the manufacturing technique of the tube (detailed in the following section); what is common among all composite tubes is the total presence of at least 5 layers, this is due to the need for tie layers bonding the structural material to the barrier layer [1] (see Figure 1.1).

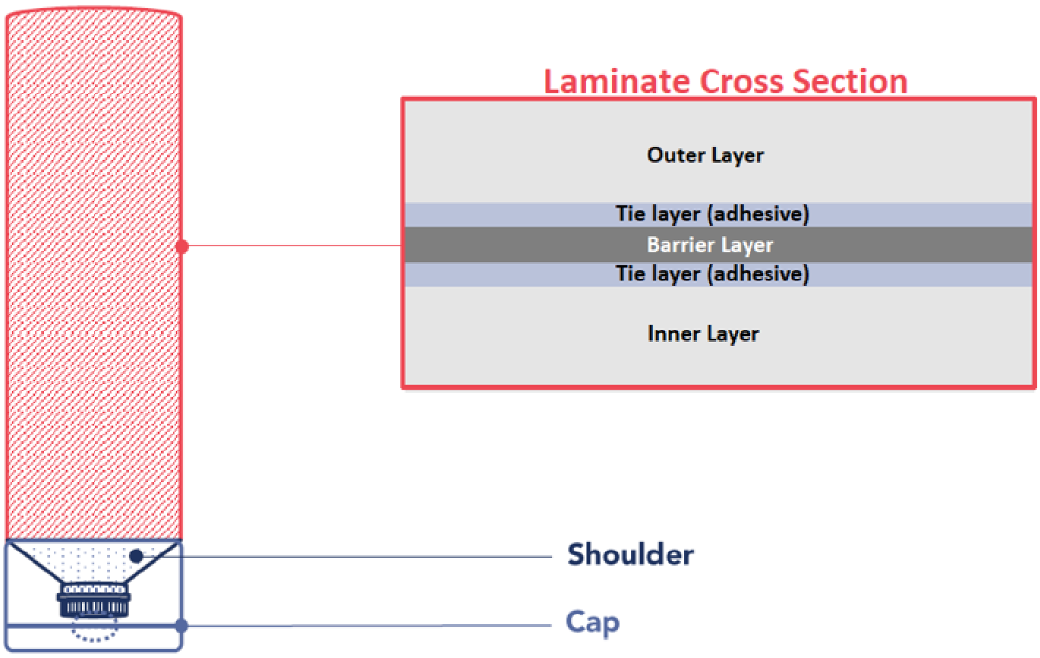


Figure 1.1. *Schematic representation of the layer structure of a laminate tube.*

1.1.3 Manufacturing of polymeric packaging tubes

For the sake of providing the reader with adequate information regarding all aspects of the tubes' life cycle (at least regarding conditioner tubes), it is deemed appropriate to briefly present the manufacturing process of extruded and laminate tubes.

1.1.3.1 Extruded tubes

The manufacturing of extruded tubes starts with the compounding of one or more resins of choice and the extrusion/coextrusion of a sleeve, which is subsequently water-cooled and cut to the proper height by a rotating knife.

The formation/welding of the shoulder can be accomplished in a series of different ways, in general, such methods are variations of conventional techniques such as compression molding (e.g. Downs process), injection molding, blow molding, or the welding of a preformed shoulder [1].

Afterwards, the tube undergoes decoration by means of offset printing, flexographics, silk screen, and/or cold foil.

Subsequently, the tube is transferred to the capping station where the cap is applied and torqued to the desired specifications.

The tube is finally ready to be filled up and sealed; an injection nozzle that dives into the tube and retracts during filling guarantees the absence of air entrapment and contamination of the sealing section.
The sealing is operated either by high-frequency induction (for ABL tubes), through a hot air system, or by means of electrically heated jaws [1][21].

1.1.3.2 Laminate tubes

The web for laminate tube production is manufactured by extrusion coating and laminating. This web is printed and made in large rolls that are slit into the proper width for tube production. [1].

The slit rolls are then shipped to the tube production facility where they are "unrolled and continuously fed through forming rolls, which very gently turn the flat material and form it into a cylinder of different diameters depending on the end customer's needs.
The sides of the material are fused together to form a long cylindrical sleeve; the sleeve advances to a cutting station where it is cut into tube bodies of the desired length" [21].

The capping, filling, and sealing steps are by all mean identical to the ones described for extruded tubes.

1.1.4 Packaging tubes sustainability

The world of packaging is rapidly transforming its products and processes to adhere to the principles of sustainability. The tube industry is perfectly on track, innovating in the fields of packaging material and tube manufacturing.

The issue of non-recyclability of ABL laminate tubes has been for the most part addresses by shifting to PBL tubes, but still, noticeable efforts are being made to reduce the amount of virgin polymeric material used in each tube:

- on one front, technical advances have allowed tube wall thicknesses to be reduced while maintaining the necessary barrier properties to protect the bulk content;
- on another front, the introduction of cellulosic materials in the layered structure is undergoing rapid development (already on the shelf);

- ultimately, efforts are been made to incorporate Post-Consumer-Recycled material and Green (bio-based polyethylene/polypropylene).

All these efforts bring the tube industry closer by the day to achieving complete sustainability [21].

1.1.5 Packaging tubes performance

The choice of a new material or a change in tube wall thickness may have different consequences on the final product properties; nonetheless, ultimately two main classes of implications can be drawn: either a difference in aesthetics and perception of the consumer or an alteration of the structural stability and integrity of the tube during manufacturing (printing for instance), transportation and shelf life; in many cases both aspects are affected.

Assessing the implications of a change in the packaging material on the aesthetics and consumer perception is of great importance in the world of cosmetic products. Nonetheless, consumer studies are needed for such evaluations, which lie outside the scope of this work.

This work will focus on the structural stability and integrity of plastic packaging when subject to external mechanical stimuli. Particularly trying to model the consequences of a deformation applied to the tube body during transportation and shelf life.

In this sense, the term performance will be used to refer to the capability of the tube to resist an external deformation, returning to its initial shape. The lesser the deformation the tube can accept (without being permanently compromised), the worse the performance. The phenomenon of permanent deformation of a tube, associated with the formation of a dent, is referred to as *denting*. Denting is an undesired phenomenon which compromises the aesthetics and, in extreme cases, the functionality of a tube; in this sense, its occurrence should be minimized, and if possible, completely prevented.

1.2 Overview of existing methodologies and models

In this section an overview of existing methodologies and models for the evaluation of packaging performance is presented; specifically, two topics will be discussed:

- standardized tests to evaluate tube deformation;
- recent developments in the modelling and simulation of packaging deformation performance.

1.2.1 Available testing methodologies for measuring tube deformation

To the author's knowledge, only a handful of testing methodologies for the measurement of tube deformation have been devised; all of them refer to the concept of the Guillotine test (for instance the European Standard EN 16285:2021, which recently substituted the EN 16285:2013).

A Guillotine test is a particular type of impact test; the procedure is the following: an empty tube is positioned on the prism-shaped support (*A* in Figure 1.2) and a predetermined weight (depending on the tube diameter) is released upon it from a fixed height. The result is a temporary compression of the tube, which is recorded on the scale and can be thus read [6].

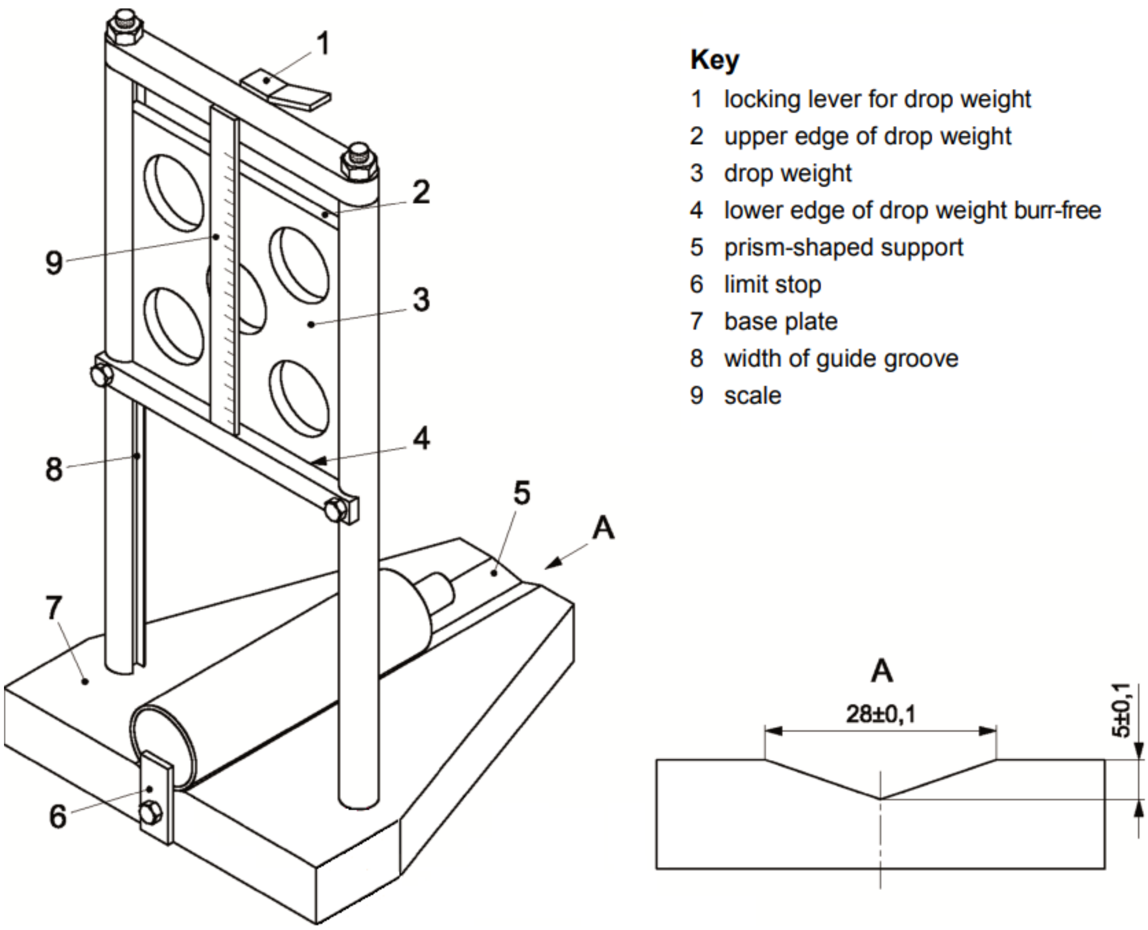


Figure 1.2. *Device for the Guillotine test for tube deformation testing [6].*

Such tests are designed to be rapid and intuitive, providing a comparative indication regarding the deformation behavior of tubes.
They can thus prove useful, for instance, to rapidly demonstrate the worsening of the mechanical properties of the tube when exposed to particular substances.

On a negative note, they only provide a rough indication regarding the performance of the tube, classifying the results in broad classes of deformation, which very likely heavily depend on the thickness of the tube and are poorly descriptive of the denting propensity of the material.

Ultimately, it is concluded that the development of a more exhaustive and informative testing methodology is worth the effort; in particular, a more articulated test can provide the capability of capturing and describing the deformation performance of each tube under the effect of stimuli of different magnitude, uniquely characterizing the tube (such a measurement could be considered as a distinctive signature of the specific item).

1.2.2 Predictive modelling of packaging deformation

Even though no other statistical study correlating the material properties of the packaging tube with its deformation performance could be identified, a great number of innovations in the general field of predictive modelling of packaging deformation have been recently proposed.

Two main approaches were identified:

- Finite Element Modelling of packages [14] and cylindrical thick wall elastic piping [28];
- Implementation of Image Correlation Techniques for the characterization of the heterogeneous strain field on the item and subsequent prediction of the constituent material mechanical properties [23][26][27].

Notice that both approaches address the complex issue of correlating the erratic geometry that commonly characterizes packages to their final deformation performance.

The approach provided in this study leverages the observation that such an effort is not needed for highly regular items such as packaging tubes; in fact, in the case of items with a standardized shape, the geometry can be fully defined by means of a very limited number of variables, and consequently, the variability in deformation performance is only dependent on such variables and on the mechanical properties of the constituent material.
Such an important observation didn't go unnoticed to this day; in fact, the phenomenon of buckling in pipings has been the focus of many studies [12][28], leading to the development of a *General Tube Equation* [12], to correlate a tube wall thickness to its deformation behavior. Notice however that the word "tube" in this instance refers to pieces of cylindric piping; thus, even if the analytical approach is highly interesting, it cannot be re-employed on the more complex geometry of the packaging tube.

It can thus be concluded that a correlation structure is proven to exist, and with the aid of multivariate modelling techniques, it can be identified and leveraged to perform predictions regarding the packaging tube deformation performance.

Chapter 2

Materials, Instrumentation, and Methods

In this chapter all materials, instrumentation (laboratory equipment and software), and methodologies (standardized mechanical tests and data analytics methodologies) that proved instrumental for the success of the project are introduced.

2.1 Materials

The only materials required for the study were tubes of different sizes and compositions, and some conditioner to fill them.
Of course, the selection of tubes had to be as varied as possible, to grant adequate explanatory and predictive capabilities to the statistical models:

2.1.1 Available tubes & nomenclature

Tubes for testing were retrieved:

- from the company's portfolio of empty tubes (currently in use or in testing phase);
- from stored samples which served as candidates but never arrived at a commercial stage;
- from discontinued products, which were still available in storage;
- from a sales point, specifically to test materials used by competitors.

The model is developed by studying a set of 14 different materials, varying in composition and thickness:

- HDPE Lam. 1 - Thickness 220/275/300/325µm;
- HDPE Lam. 2 - Thickness 330µm;
- PE/PET - Thickness 390µm;
- ABL - Thickness 390µm;
- PP - Thickness 260/290µm;
- Shop Tube 1 - Thickness 330µm;

- Shop Tube 2 - Extruded tube - Thickness 350/480µm;
- Shop Tube 3 - "Paper" composite - Thickness 360µm;
- Shop Tube 4 - Extruded tube - Thickness 470µm.

2.1.2 Conditioner

As a consequence of the discoveries presented in the study regarding the influence of each different factor, there was no need for experimenting with a multitude of conditioners; only one kind was needed.
For confidentiality reasons not much can be disclosed about the conditioner used for the study; nonetheless, for the sake of the presentation, it is sufficient to know that it is characterized by average physical properties (among conditioners), with a viscosity of around $10^4 cP$.

2.2 Instrumentation

In this section all instruments which have been used for the study are listed and briefly discussed; this includes mechanical testers and software for data analytics.

2.2.1 Mechanical testers

Mechanical testers are the main source of data in this study: they were used to run standard tensile and bending tests (TA DMA-Q800) and to quantify the mechanical resilience of tubes (Zwick AllroundLine).

2.2.1.1 TA DMA-Q800

Let's refer to the manufacturer descriptions to illustrate the functionalities of the TA DMA-Q800 (Figure 2.1(a)):

"The Q800 is the world's best-selling DMA, for very good reasons. It utilizes state-of-the-art, non-contact, linear drive technology to provide precise control of stress, and air bearings for low friction support. Strain is measured using optical encoder technology that provides unmatched sensitivity and resolution. With its unique design, the Q800 easily outperforms competitive instruments, and is ideal for high-stiffness applications including composites" [19].

An important peculiarity of the instrument, as described in the previous paragraph, is that it works by imposing a force and measuring the consequent strain on the sample. All mechanical tests executed with the machine will thus be imposed-force tests; nonetheless, the mechanical curves will always be displayed with the elongation measure on the abscissa, to conform with the most common representation of force-elongation test results (related to imposed-deformation tests).

Choice of the instrument

Strips or dumbbell-shaped samples cut from tubes tend to retain the original curvature of the tube/roll they are sourced from. This is a problem when bending tests need to be performed, since they can be heavily and unpredictably affected (the sample should be straight in all directions).
The issue can be limited through a thoughtful sample preparation:

- cutting the samples along the non-curved direction of the sheet, this produces straight samples with a slight curvature on the short side;
- reducing the sample size up to the point in which the curvature across the short side of the sample is no more appreciable.

This led to the use of 2mm wide rectangular and dumbbell-shaped samples for the mechanical tests (discussed in more detail in Section 2.3).
A further advantage of such small samples is that many can be cut from a single sheet, in case not many sheets/tubes of the specific material are available.

The TA DMA-Q800 can be used to perform tensile and bending tests on such samples, granting high-precision results with the added benefit of a controlled temperature environment.

Tools and accessories

To perform tensile and three-point-bending tests on the TA DMA-Q800, the two corresponding kits need to be installed on the machine.

2.2.1.2 Zwick AllroundLine

The AllroundLine (Figure 2.1(b)) is the most customizable and versatile machine offered by the company for static material testing [29].

Choice of the instrument

The Zwick AllroundLine has been the tester of reference to perform custom mechanical tests on tubes. This is due to its great flexibility when it comes to settings and testing routine, which allows to design and execute reliably rather complex tests.

Tools and accessories

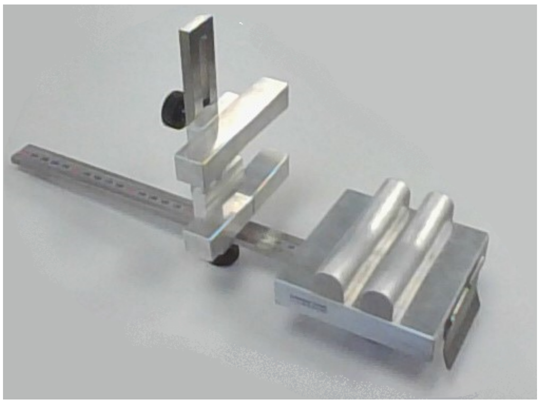
To perform the mechanical tests on the Zwick AllroundLine, a series of accessories are employed:

- load cell: Xforce HP 0.5kN;

- tube holder (custom device, see Figure 2.1(c));
- rounded pressing head (see Figure 2.1(d)).

(a) *TA Instruments DMA-Q800 equipped with tensile testing accessories.*

(b) *ZwickRoell AllroundLine universal static tester.*



(c) *Denting test custom tube holder for the Zwick AllroundLine.*

(d) *Denting test pressing head for the Zwick AllroundLine.*

Figure 2.1. *Mechanical testers and accessories.*

2.2.2 Software

The raw data retrieved from the testing machines would be useless without adequate software support to pretreat it (Spyder), analyze it, and plot the results (JMP).

2.2.2.1 Spyder (version 5.1.5)

Spyder is an open-source cross-platform integrated development environment (IDE) for scientific programming in the Python language.

The software was instrumental for data pretreatment and visualization (according to the algorithms described in Section 3.3).

2.2.2.2 JMP (version 16.1.0)

JMP is a suite of computer programs for statistical analysis developed by JMP, a subsidiary of the SAS Institute.

Thanks to its repertory of in-built modelling techniques and a vast range of visualization options, it proved to be a reliable tool to design experiments, analyze data and develop models.

2.3 Standard mechanical testing methodologies

To characterize tube materials, standard mechanical tests are performed; ASTM standards are used as a reference, but could not be followed in regards to a few aspects, such as sample size (for the issue of the inherent bending of the material discussed in Section 2.2.1.1). Nonetheless, much care was used to ensure that the deviations from standard methodologies didn't pose a risk to the quality of the results.

2.3.1 Room Conditions

The laboratory atmosphere is maintained in standard conditions: 23±2°C and 50±5% relative humidity.

2.3.2 Sample preparation

The samples consist of rectangular strips or dumbbell-shaped specimens cut perpendicularly to the direction in which the sheet curves; tensile tests were nonetheless performed also on samples cut in the other direction, to verify the assumption of isotropic behavior.
The edges of the samples should be sharp, without signs of delamination or incisions.

Regarding tube geometry:

- **width**: 2mm, measurements obtained from slightly wider or narrower samples can be normalized to 2mm during data pretreatment; the difference in width from top to bottom should not exceed 0.01 mm.

  A small value of the width:

  - allows to produce samples that are straight in both main directions;
  - reduces the number of sheets needed to produce the samples;
  - grants that the sample can be yielded within the force limit of the instrument.
- **length**: 40-35mm; needs to be sufficient to comfortably clamp the sample on the tester.

The same sample geometry proved to be adequate both for bending and tensile tests.

While at the beginning of the project samples were produced in the form of strips, some of the last tested samples were created through a dumbbell cutter; this improvement:

- grants repeatability and speed in sample production;
- ensures a constant width (2.10mm at the neck);
- ensures a constant length of the sample (35mm).

Nonetheless, checking the quality of each sample remains of paramount importance.

It was verified that the results obtained testing dumbbell-shaped samples are equivalent to the ones obtained testing the previously described rectangular strips; it follows that the first option is viable in case of absence of an adequate dumbbell cutter.

2.3.3 Tensile Tests Procedure

The methodology of reference for the tensile tests is the ASTM D882-18 [5] and the relative referenced documents. Details regarding the tester settings and the deviations from the standardized methodology are here described:

2.3.3.1 Procedure

The machine must first of all be calibrated after installing the tensile test accessories.

Subsequently, the sample should be fixed in place; the following details should be verified:

- the printed face of the sample should always face the same direction;
- the sample should be fixed as centrally and straightly as possible;
- the side of the clamps with grips (not flat) must be used to hold the sample;
- the bolts of the clamps should be screwed with a torque of 5 in-lb;
- the gap between the two clamps must be around 10mm.

To obtain consistent results, the first recommendation is particularly important, namely to ensure that during the test the sample is straight; this means that its main axis should be parallel to the direction of traction; to achieve this, a procedure is suggested:

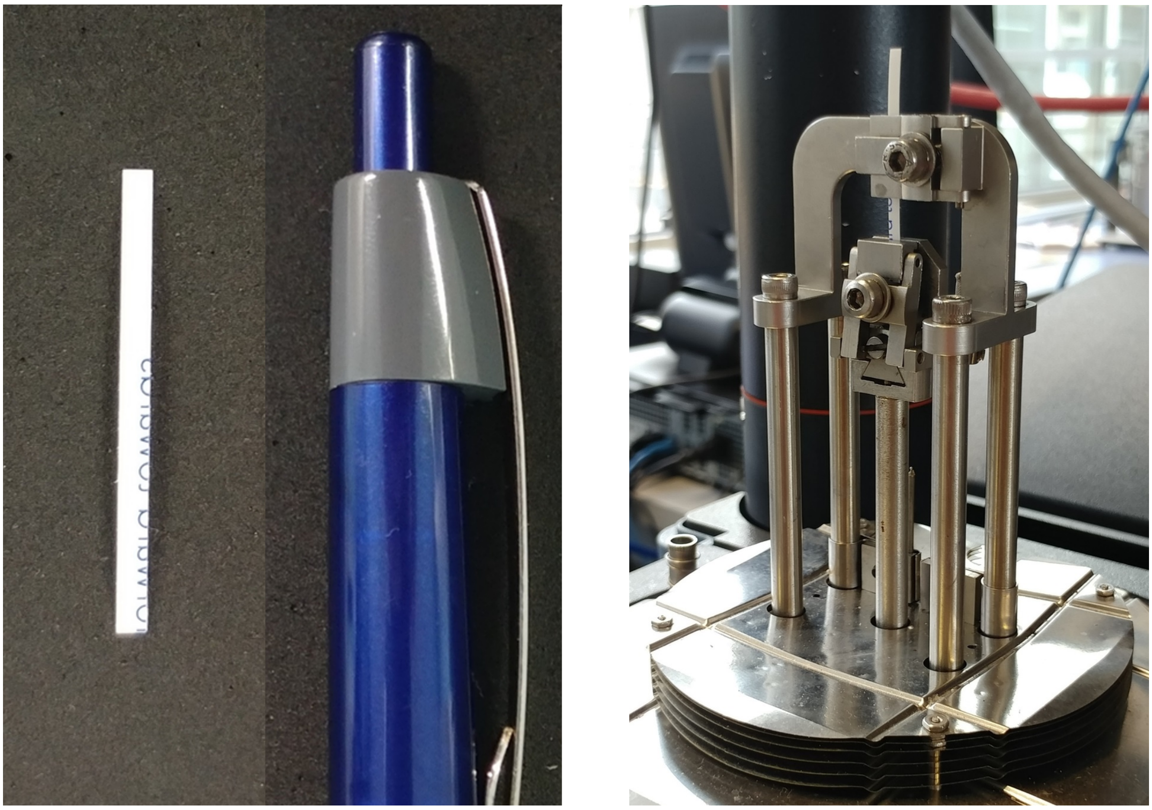
- ensure that the bottom clamp is exactly below the top one (this can be adjusted by unscrewing the bolt that keeps it still and adjusting its position, making sure to screw the bolt firmly after the adjustment);
- position correctly the sample:
    1. open both clamps;
    2. insert the sample between the two clamps being careful that the bottom extreme does not contact the screw of the bottom clamp (such contact would cause the bending of the sample upon screwing), keep the sample in place pressing softly on the bottom clamp;
    3. move the bottom sled up and down, the sample should slide in between the top clamp remaining centered with respect to the top referral line (a line present on the top clamp exactly to help in adjusting the sample);
    4. when sure that the sample is exactly straight (very important, even slight bending implies pronounced differences in the results) carefully screw the bottom bolt;
    5. check again sample straightness by repeating point #3; if the sample is not straight, discard it and start from point #1;
    6. screw the bolt of the top clamp (ensuring that the distance between the clamps is around 10mm).

After fixing the sample, the "controlled force - stress/strain" test can be run; the specifications and steps of the test are presented:

- imposing a pre-load of 1N;
- equilibrating the temperature at 23°C and waiting 1 minute for the system to get to isothermal conditions;
- ramping up force by 3N/min up to 18N.

Three tests are conducted on each material to assess the variability of the measurements. Further testing is needed in case the normalized standard deviation of the three measurements is over 5%.

Specimens that display obviously faulty behaviors shall be discarded and replicas operated. However, jaw breaks (failures at the grip contact point) are acceptable if it has been shown that



(a) *Side-by-side comparison of a sample of tube material and a pen.*

(b) *DMA-Q800 equipped with tensile testing accessories ready for a run.*

Figure 2.2

results from such tests are in essential agreement with values obtained from breaks occurring within the gauge length.

2.3.4 Bending Tests

The methodology of reference for the bending tests is the ASTM D790-17 [4] and the relative referenced documents; moreover, useful indications were found in Nasa's Technical Note D3270 [16]. Details regarding the tester settings and the deviations from standardized methodologies are here described:

2.3.4.1 Procedure

The machine must first of all be calibrated after installing the three-point-bending test accessories.

Subsequently, the sample should be positioned as centrally and straightly as possible on the holders, removing slight distortions it might have acquired (if the distortions are pronounced the sample is to be discarded).

The printed side of the sample should be faced upwards, this grants repeatability of the experiment for materials that possess a slight asymmetry in the layered structure. Such asymmetries in fact might entail a variation in the bending properties depending on the tested side of the sample.

After positioning the sample, the "controlled force - stress/strain" test can be run; the specifications and steps of the test are presented:

- imposing a pre-load of 0.001N;
- equilibrating the temperature at 23°C and waiting 1 minute for the system to get to isothermal conditions;
- ramping up force by 0.5N/min up to 18N.

Three tests are conducted on each material to assess the variability of the measurements. Further testing is needed in case the normalized standard deviation of the three measurements is over 5%.

Specimens that display obviously faulty behaviors shall be discarded and replicas operated.

2.4 Mathematical methodologies

Mathematical methodologies for multivariate statistic analysis are at the core of the project, in fact, all the modelling efforts here presented are possible thanks to the existence of data analytics techniques such as Prinicipal Component Analysis and Partial Least Square Regression, which are powerful yet well-known and reliable tools in the hands of the analyst.

Such techniques will be briefly presented in this section together with some metrics used to evaluate the variability of data and goodness of fit of a regression model.
Concepts such as mean and standard deviation will instead be considered as acquired.

2.4.1 Metrics for evaluation of variability and goodness of fit

Different metrics exist for the evaluation of the variability of data and the goodness of fit of a model:

2.4.1.1 Coefficient of Determination (R^2)

The coefficient of determination R^2 is the main metric for the evaluation of fit quality when it comes to linear regression.

For this reason, it is broadly used in actual-by-predicted plots as well as in multivariate linear models (in the form of adjusted R^2 to account for the presence of multiple independent variables).
It is instead been proven to not be reliable when it comes to non-linear regression [18].

It is given by:

$$R^2 = 1 - \frac{SS_{res}}{SS_{tot}} \tag{2.1}$$

$$SS_{\text{res}} = \sum_i (y_i - f_i)^2 = \sum_i e_i^2 \tag{2.2}$$

$$SS_{\text{tot}} = \sum_i (y_i - \bar{y})^2 \tag{2.3}$$

Where:

R^2 = Coefficient of Determination
SS_{res} = Residual Sum of Squares
SS_{tot} = Total Sum of Square
y_i = observed values
f_i = predicted values
e_i = residuals
$\bar{y}$ = mean of the observed values

Based on its definition, it can be concluded that R^2 represents the fraction of the variance explained by the model; in this regard, it has the very interesting feature of being bounded between zero and one. The R^2 does not have a unit of measure and provides an absolute indication of the quality of the fit.
In the case of non-linear regression, other metrics can be used to evaluate the goodness of fit; even though these metrics are not bounded as the R^2, they can still prove reliable in comparing models or evaluating the regression quality.

2.4.1.2 Coefficient of Variation (CV or RRMSE)

The Root Mean Square Error is the standard deviation between measurement and prediction:

$$RMSE = \sqrt{\frac{\sum_{i=1}^{n} (y_i - f_i)^2}{n}} \tag{2.4}$$

Where:

n = Number of observations

Its value is related to the magnitude of the values of the observations, thus stand alone it is meaningless. For this reason, it is common to refer to the Relative Root Mean Square Error (RRMSE), defined as the ratio between the RMSE and the average of the observations.

$$RRMSE = \frac{RMSE}{\bar{y}} \tag{2.5}$$

Note that this operation doesn't impose any bound on the new metric, which can potentially grow to infinite. Nonetheless, for a good fit, it is expected that the RRMSE represents only a few percentage points, namely that the standard deviation of the fitted points is only a small fraction of the mean of the observed values.

A disadvantage of this metric is that it heavily depends on the average of the observed values; for instance, if two sets of points with a different mean are to be fitted (independently from each other), given that the actual quality of the two regression models is similar, the RRMSE favors the fit with the smallest mean value.

2.4.1.3 Normalized Root Mean Squared Error (NRMSE)

This issue can be addressed by adopting a different normalization factor for the RMSE; the NRMSE basically is the ratio of the RMSE and an arbitrarily chosen value, commonly the greatest among the observed values.

When comparing the fit of a non-linear model on different sets of points, given that all sets vary in the same range, the NRMSE proves to be the most reliable metric to evaluate (and compare among curves) the quality of the fit.

2.4.2 Statistical Design of Experiment

The Statistical Design of Experiments is a methodology to organize and plan a reduced number of experiments to obtain a meaningful evaluation of the impact of a set of factors on one or more response variables. This can be achieved by developing a linear regression model which accounts for the influence of each factor and an adequate set of interactions, to then statistically evaluate (through the ANalysis Of VAriance) the relevance of each contribution, excluding the ones that are negligible. Finally, the study of the relevant factors and interactions allows to generate response surfaces and main interaction plots to rapidly assess the impact of a change in the factors' values or to explore their domain, to identify the optimal configuration for a specific task [20].

2.4.3 Principal Component Analysis

Principal Component Analysis [9] is at the basis of multivariate statistical analysis.

Data pretreatment and autoscaling, even though fundamental to correctly perform the analysis, were deemed not worth discussing, since they are not essential to deliver the ideas at the basis of PCA (and PLS).

Let's start by providing a conceptual framework: given a set of V variables characterizing a group of N observations, these variables are often correlated to each other, meaning that, to some extent, their value is dependent on the value of the others. Let's focus on a single observation to represent the situation in a Euclidean space: the variables can be represented as non-orthogonal axes departing in different directions from an origin, meanwhile, the observation is a point in the space defined by the axes; each variable, as long as it is not linearly dependent on the others, introduces a new dimension to the Euclidian space, but the extent to which this new axis trespasses in the new dimension might be limited; if this is the case, it means that the variable actually brings little information that could not already be described in terms of the previously introduced variables (axes). This phenomenon is known as collinearity, and is one of the main problems that PCA can address.

The PCA methodology identifies a new axis within the V-dimensional space of the variables, along which the covariance of the observations is maximized (maximization problem); such axis is therefore the direction in which the data exhibits the greatest variability (first principal component). The solution to the maximization problem outputs the projections of the variables (of the versors of the original axes) on the newly identified direction of maximum variability; such values are called *loadings* (p_1) and indicate to which degree each of the original variables is related to the principal component.

$$\begin{cases} \underset{p}{max}(p_1^T X^T X p_1) & \longrightarrow \text{ optimality condition} \\ s.t. \;\; p_1^T p_1 = 1 & \longrightarrow \text{ orthonormality condition} \end{cases} \tag{2.6}$$

Where:

X = data matrix [N observations x V variables]

The observations are then projected on the principal component, identifying the *scores* ($t_1 = Xp_1$). The scores are representative of the observation in the newly identified monodimensional space.

The projection of the variables on a single vector (the first principal component) is often not enough to capture an adequate fraction of the data variability; the method is thus iterated, first reconstructing for each variable the *residuals* E_1 (namely the difference between the original values of each variable and the projections on the principal component $E_1 = X - \hat{X}_1 = X - t_1 p_1^T$), and then proceeding to identify a second main direction of variability within the residuals. The extraction of principal components can be iterated R times, where $R = rank(X)$:

$$X = \sum_{a=1}^{R} t_a p_a^T = TP^T + E \tag{2.7}$$

Nevertheless, for the method to be practically useful, it is iterated until an adequate fraction of the variability is captured by the model (A times):

$$X = \sum_{a=1}^{A} t_a p_a^T + \sum_{a=A+1}^{R} t_a p_a^T = TP^T + E \tag{2.8}$$

Numerous methods for the selection of the optimal number of principal components have been proposed, among which:

- scree test [2];
- eigenvalue-greater-than-one rule [13];
- cross-validation [24].

Briefly said, PCA allows to describe the original dataset, made of a high number of collinear variables, with a low dimensional space of principal components. The method is extremely useful in developing an understanding of highly complex systems, since the principal components are often associated with the real causes of the variability in the data; thus by means of ingenuity and leveraging the knowledge of the involved phenomena, it is possible to interpret the correlation structure identified by the loadings. Then, by studying the scores of each principal component, the method allows a precise characterization of the individual observations.

The newly developed space of principal components can be also used to conduct an outlier analysis:

- the distance of the observations' projections from the origin of the principal components can be studied (Hotelling's T^2 statistic); it means evaluating abnormal behaviors **within** the latent space [11];
- the orthogonal distance of the observations **from** the latent space can be studied (Q statistic); it means identifying observations that are interested by phenomena which are not explained by the model.

2.4.4 Partial Least Square Regression

Partial Least Square Regression (PLS) is a linear multivariate statistical method capable of correlating two data matrices (data matrix of the predictors X [N observations x V variables] and data matrix of the responses Y [N observations x M variables]); the technique exploits the typical ability of multivariate methods to analyze many noisy and collinear data [9].

2.4.4.1 Key concepts and algorithm

To a great extent, the methodology implements the same strategies discussed for PCA (Section 2.4.3) to conceptually define (for both data matrices) directions of maximum variability, loadings, and scores; the difference lays in the formulation of the maximization problem, which becomes the identification of the direction of maximum variability of X that best predicts Y:

$$\begin{cases} X = \sum_{a=1}^{A} t_a p_a^T + E = TP^T + E \\ Y = \sum_{a=1}^{A} u_a q_a^T + F = UP^T + F \\ u_a = b_a t_a \end{cases} \tag{2.9}$$

Where:

T & U = respectively predictors and responses scores;
P & Q = respectively predictors and responses loadings;
E & F = residuals;
A = number of latent variables of choice;
b_a = regression coefficients $\left(b_a = \frac{u_a^T t_a}{t_a^T t_a}\right)$.

The problem is commonly solved by the NIPALS algorithm (calculates recursively the PLS parameters).

In order to obtain orthogonal predictors scores, as in the PCA, it is necessary to introduce weights (coefficient of the linear combination of X which determines the predictors scores $t_1 = Xw_1$); the weights of the first latent variable (w_1) are obtained by solving the following maximization problem:

$$\begin{cases} \max_{w_1}(w_1^T X^T Y Y^T X w_1) & \longrightarrow \text{ optimality condition} \\ s.t.\ \ w_1^T w_1 = 1 & \longrightarrow \text{ orthonormality condition} \end{cases} \tag{2.10}$$

The subsequent steps are:

- the evaluation of the residuals after the extraction of the first latent variable (deflating X and Y matrices):

$$\begin{cases} X_2 = E_1 = \left(I_N - \frac{t_1 t_1^T}{t_1^T t_1}\right) X \\ Y_2 = F_1 = \left(I_N - \frac{t_1 t_1^T}{t_1^T t_1}\right) Y \end{cases} \tag{2.11}$$

- the iteration of the procedure to extract as many latent variables as deemed appropriate:
    1. determination of the weights w_a^* orthogonal to the ones of the previous $(a-1)$ step;
    2. calculation of the predictors scores $t_a = Xw_a^*$
    3. evaluation of the residuals E_a and F_a by deflating X_a and Y_a

In short, PLS methodology identifies the directions of maximum variability of the predictors and rotates them to maximize covariance with respect to the direction of maximum variability of the predictors.

2.4.4.2 Correlation structure interpretation

The correlation structure between the main directions of variability in the predictors and the responses can be interpreted in causal terms thanks to an adequate knowledge of the involved phenomena. Such interpretation can be performed through an attentive study of scores, loadings, and residuals:

- **T and U scores**: projections of the observations on the latent space; they allow to characterize the observations in terms of latent variables (instead of the original variables), and thus to identify differences and peculiarities within the predictors (T) and responses (U);
- **P and Q loadings**: linear combinations of the original variables that constitute the latent variables; they provide information regarding the contribution that each original variable brings to a latent variable; they are instrumental for the interpretation of the data correlation structure (identification of fundamental phenomena driving the data variability);
- **E and F residuals**: represents the fitting error (minimized in the least square sense); they define the distance of the observations from the model hyperspace.

Similarly to PCA, Hotelling's T^2 [11] and Q statistics can be evaluated and interpreted to perform an outlier analysis.

2.4.4.3 Model validation

Four aspects are assessed to verify the meaningfulness of a regression model (and the adequacy of the chosen latent variables):

- **quality of the fit**: can be evaluated through the Determination Coefficient R^2;
- **meaningfulness of the terms in the regression model**: granted when the identified latent variables are meaningful, meaning that they represent a considerable fraction of the data variability and can be convincingly proven to be correlated to mechanisms involved in the studied phenomenon;

- **appropriateness of the data**: an outlier analysis can be perfored to identify deviating sample and consider their exclusion from the model;
- **appropriateness of a linear model structure**: can be verified thorugh an attentive study of the trends in t_a versus u_a plots.

2.4.4.4 Predictive and prescriptive modelling

Having ensured the quality of the model and developed a proper understanding of the correlation structure within the data, the model can be used to perform predictions: if a new observation within the predictors dataset is available, it can be projected on the space of the latent variables to then estimate the response:

$$t_{NEW} = x_{NEW} P \tag{2.12}$$

$$\hat{y} = b \ t_{NEW} Q^T \tag{2.13}$$

It's worth noting that high-quality predictions can be performed by models with a marked explanatory capability with respect to the responses.

Similarly, a new observation within the responses dataset can be originated (desired/optimal response) to then predict the corresponding set of predictors (model inversion). In this case, high-quality estimates are obtained from models with a marked explanatory capability with respect to the predictors.

Chapter 3

Results

In this chapter, the conceptual and practical results of the study are described. Even though such results are often interlinked, it is possible to identify six main achievements:

- the development of a conceptual framework;
- the definition and validation of a testing methodology to quantify the denting phenomenon;
- the development of software for the automatic management of the raw data retrieved from the experiments;
- the identification of a set of main variables involved in tube denting through the statistical design of experiments;
- the development of a predictive model to evaluate the denting performance of a tube from the mechanical properties of the constituent material;
- the proposal of a denting index to easily quantify denting performance, and of a diagram to compare denting indices of different tubes.

All the points here listed are tackled individually in the following sections:

3.1 Conceptual framework

The first achievement of the study consists in a conceptual scheme which frames the problem (Figure 3.1), allowing to identify a strategy to solve the issue, and, more generally, to approach problems of similar nature.

3.1.1 Variables

The first step taken in approaching the problem is the identification of the variables which might potentially have an impact on the denting phenomenon.

It is of great importance to identify only quantitative variables; this is essential to then specify the domain of the study and to obtain broad predictive capabilities. For instance, information such as the names of the materials composing the tubes needs to be led back to the specific

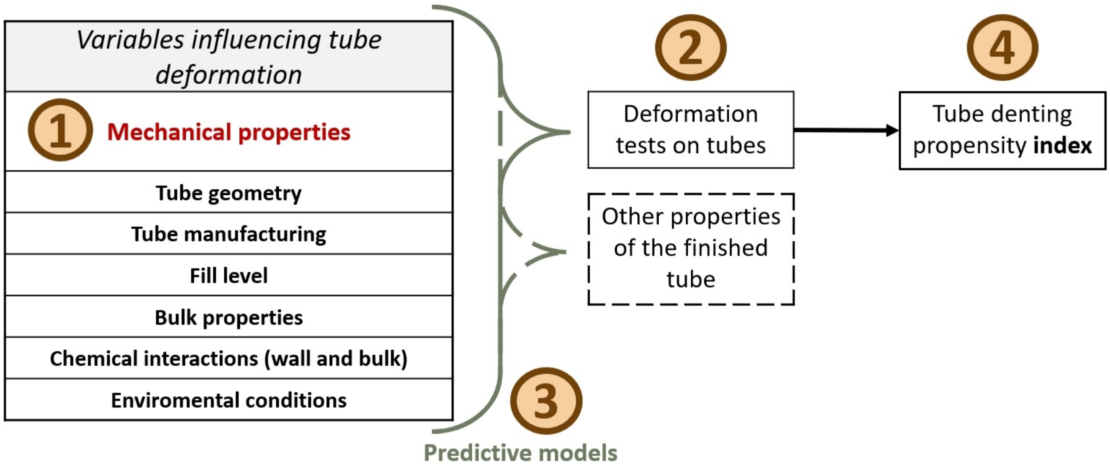


Figure 3.1. *Schematic version of the conceptual framework.*

mechanical properties of such materials.

For simplicity, the identified variables are summarized in classes and listed in Table 3.1.

Table 3.1. *Variables influencing the mechanical response of a tube.*
In blue variables related to the tube wall, its geometry and manufacturing; in yellow variables related to the bulk fluid; in green variables related to both; in red variables related to ambient conditions.

Grouping	**Variables** influencing the **mechanical response** of a tube
Mechanical properties	Intrinsic material properties of outer layer Intrinsic material properties of barrier layer Intrinsic material properties of inner layer Thickness of the outer plastic layer Thickness of barrier layer Thickness of the inner plastic layer
Geometry	Tube diameter Tube body height
Tube manufacturing	Extruded or Laminate Internal pressure after sealing
Fill level	Bulk fill level
Bulk properties	Vapor pressure Dynamic viscosity of bulk (at small shear stresses)
Chemical interactions (wall and bulk)	Activities of mobile components in each phase Diffusivities of mobile components in tube wall Chemical reactions
Enviromental conditions	Temperature Pressure Air absolute humidity

Each variable influences the denting performance to a different degree and through peculiar mechanisms:

- **Mechanical properties of the tube wall**

  Tube walls are made of composite materials; thus, their mechanical properties and ultimately their performance depend both on the combination of materials used and on the thickness of each of the layers:

  - <u>Thickness of the individual layers</u>
  - <u>Intrinsic mechanical properties of the individual layers</u>

  The study of the mechanical properties of a composite material is a complex topic; both analytical and experimental approaches are available.

  Regarding the first category, it is possible to derive some extrinsic properties of a layered material from the intrinsic property of the constituents and their thickness. Such methods are mainly related to the prediction of stiffnesses [25], while properties in the plastic range are more difficult to generalize and thus predict. The problem with analytical derivations is that the results are often not reliable, this is because:

  - often the properties of the layers change during manufacturing;
  - even very thin layers (not accounted for) can change profoundly the final values of the predicted property of the layered material. This is true for coatings, adhesives, surface finishes etc...

  This renders analytical results unappealing as variables for modelling, at least without introducing some correlations in the equations for their derivation.

  The experimental approach can directly provide information on the mechanical properties of the composite material without prior knowledge of its structure and composition, this means that it is more readily applicable. Moreover, it is more accurate, and the results are more informative (including both the elastic and plastic range); nonetheless, some difficulties are still present, such as:

  - the existence of a multitude of standardized types of tests for the measurement of each flexural and tensile property;
  - the necessity to take into account the anisotropic nature of certain materials, thus the dependence of the results on the orientation of the sample;
  - each test is only valid for the specific combination of materials and thickness; namely the obtained properties are extrinsic (like stiffness), intrinsic properties like rigidity are meaningless in the case of composite materials. This means that a great number of experiments are needed if a multitude of samples is available, resulting in a considerable effort in terms of time and resources (in comparison with a purely analytical approach).

- **Geometry of the tube**

  Apart from the material, the form of the item is of paramount importance to determine how it will deform under stress. The regular shape of tubes greatly simplifies the problem, allowing to fully characterize their structure by only fixing two scalar variables:

  - <u>Diameter</u>

    The diameter of tubes for use in Hair Care Packaging is usually either of 40mm or 50mm. In some rare cases, it can reach 60mm. Tubes with other functions can have even smaller diameters (toothpaste for instance is often around 30mm).

  - <u>Body height</u>

    It is reasonable to measure tube height referring to the length of the body (excluding the shoulder and the cap). This allows to compare tubes that have different caps. Tube body height in Hair Care Packaging applications generally varies between 100 and 200mm.

- **Tube manufacturing**

  Even using the same geometry and materials, the process through which a tube is manufactured can have a deep impact on the tube final properties:

  - <u>Extruded or laminate</u>

    laminate tubes have weld lines, which extruded ones do not; such lines might constitute a weaker/stiffer point in the deformation of the tube.

  - <u>Internal pressure after sealing</u>

    Sealing technique, device, and ambient conditions influence the amount of air included in tubes and ultimately the internal pressure; practically this means sealing the tube in a cooler environment, at a lower ambient pressure or simply pre-forming the tube before sealing it. A puffed-up tube might prove significantly stiffer than a deflated, but otherwise identical, one.

- **Fill level**

  Finished tubes contain air and bulk fluid in different proportions. Air, differently from the bulk fluid, is compressible. This can make a partially empty tube easier to permanently deform than fully filled one.

- **Bulk fluid properties**

  The bulk fluid itself can influence the permanent deformation of a tube in a number of ways:

- Dynamic viscosity

  Tubes containing fluids with a viscosity significantly different from one another might respond differently to external loads;
- Vapor Pressure

  Bulk fluids containing volatile substances (ethyl alcohol for instance) might develop internal pressures which are significantly higher than the ambient one; this renders the tube particularly stiff and prevents permanent deformation; it is important to consider that such a property of the bulk fluid must be accounted for, since it might cause issues to the consumers during usage.

- **Chemical interaction among bulk fluid and tube wall**

  Filling up the tubes with bulk fluid not only has mechanical implications, but also leads to chemical interactions. The tube wall and the fluid bulk represent two phases, which tend to a chemical equilibrium; this specifically means that molecules from the bulk migrate by simple diffusion into the tube wall and vice versa (additives contained in the polymers can migrate into the bulk). This change of composition in the tube wall can have profound effects on its mechanical properties.

  Achieving chemical equilibrium takes time, the conformation of the polymeric phase in the tube wall (for instance the presence of micro-crystalline domains) can hinder the migration of chemical species.

  Without diving into the topic, let's list the properties which should be studied to understand and model these phenomena:

  - Activity coefficients of the bulk fluid components in tube wall layers and in the bulk fluid
  - Activity coefficients of the polymer additives in tube wall layers and in the bulk fluid

    These properties allow to evaluate chemical equilibrium conditions between the two phases;
  - Diffusivity of bulk fluid components in tube wall layers
  - Diffusivity of the polymer additives in tube wall layers

    These properties allow to evaluate the kinetics of the transport phenomena of substances being transferred out and into the tube wall. Assuming that the transport in the tube wall is much slower than the one in the bulk fluid, only the tube wall layers' diffusivities are relevant.

    These problems are the exact reason why the presence of a barrier layer, either polymeric or metallic, is needed in the structure of a tube wall: barrier layers prevent active ingredients, humidity, fragrances, etc. to diffuse out of the container, as well as oxygen to permeate into the fluid.

- Chemical reactions between tube wall layers and bulk components

  Significant chemical reactions among components of the finished tube should not happen; such phenomena only take place as a design mistake.

  An example of an undesired chemical reaction leading to tube performance degradation could be the red-ox reaction between the aluminum barrier layer in ABL tubes and reactive ingredient migrating from the bulk through the polymeric layers of the tube.

  A similar event would lead first and foremost to the delamination of the tube wall layers, with profound degradation of the tube's mechanical stability and impermeability. Moreover, the side products of the reaction are unknown, this would imply unknown effects on the properties of the bulk fluid.

The change in time of tube and bulk properties is undesirable and many efforts are put in place to prevent or slow down these processes as much as possible. An appropriate choice of materials and bulk fluid components is key. Nonetheless, given the long shelf life of the products, it is clear that, to some degree, these phenomena are unavoidable.

All of these aspects are scrupulously tested by the company for each new packaging solution; this is of paramount importance for a multitude of reasons:

- granting bulk fluid quality and safety;
- granting the performance during manufacturing, transportation, shelf life, and usage of the packaging;
- acquiring a deep understanding of the phenomena associated with packaging is fundamental for the rapid and effective development of new packaging solutions.

- **Ambient conditions**

  Ambient conditions comprehend all those external factors which interact with the item of the study and influence its characteristics.

  - Temperature

    Ambient temperature affects tube deformation indirectly, by inducing changes in almost all the above-mentioned variables. The variables which are mostly affected by changes in temperature are:

    * intrinsic mechanical properties of the individual layers;
    * internal pressure after sealing;
    * bulk fluid properties.

– Pressure

Ambient pressure can vary during transportation (across mountains or by plane), reaching for instance pressure gradients of 0.38 bars at altitudes of 3660 meters (assuming manufacturing at sea level) [15].

Ambient pressure affects tube performance mainly by inducing deformations due to the difference in pressure with respect to the internal pressure of the tube.

– Absolute humidity

Absolute humidity affects the mechanical properties of the tube. This is a consequence of the establishment of chemical equilibrium between water vapor in the air and in the tube wall. The mechanical properties of hygroscopic polymeric material can be significantly altered once equilibrium is reached.

For a quantitative evaluation of the transport and equilibrium in each layer, the same properties studied for the interaction between bulk fluid and tube wall can be considered in this instance.

These aspects are even more important for tubes including cellulosic materials.

3.1.1.1 Notes on variables interaction

It is interesting to notice that many variables are influenced by ambient conditions; this is undesirable in the description of a phenomenon, but difficult to avoid since a generally valid law which allows the decoupling of these variables is not available.

This is the case of the dependence of many properties in the list on temperature (intrinsic mechanical properties, viscosity, vapor pressure...); even though empirical correlations which decouple these properties from temperature may be available, they are not generally valid, and thus would already restrict the domain of the study, which should be avoided at this stage.

Another noteworthy aspect is the relationship among ambient pressure, internal pressure after sealing, and vapor pressure of the bulk (function of ambient temperature); these variables all ultimately influence a single parameter: the pressure gradient between the inner and outer sides of the tube, which then affects the propensity of the tube to accommodate deformations.

3.1.2 Screening test for sensitivity analysis

Not all the identified variables have a significant impact on denting performance. This is important, since it makes it possible to reduce significantly the complexity of the study by identifying a set of key variables and performing a sensitivity analysis only on them.

A screening test has to be designed and performed to identify the key variables. Moreover, depending on the objectives of the study, the value of some impactful variables can be fixed to an arbitrary value. These choices will constitute limits of the model, which is important to consider when performing predictions.

The details regarding the specific screening test design and the related results lie outside the description of the conceptual framework and will consequently be discussed separately.
It is worth noting that, for the study of a different aspect of tube performance (not denting), a conceptual approach similar to the one here described could be taken, but considering a different set of key variables.

3.1.3 Measurement of selected key variables

Among the most impactful variables, some may be readily quantifiable, while others might require measurements (mechanical properties, bulk properties, etc...). For studies regarding the mechanical performance of a tube, generally, the mechanical properties of the material are impactful.

3.1.3.1 Measurement of material mechanical properties

Once determined that, as expected, material properties actually have a significant impact on the phenomenon under study, a design of experiment is developed and the measurements are performed.
Care should be taken in ensuring that:

- all materials under study can be considered isotropic (no difference in the results upon changes in the direction along which the tested samples are cut);
- the layered structure of the materials is symmetric or quasi-symmetric; meaning that, starting from the central layer of the composite material, the sequence of layers repeats in an almost identical way in terms of thicknesses and materials in both directions. This is important in regard to bending measurements.

These conditions can be verified either by performing some tests or can be assumed thanks to prior knowledge of the materials.
If such conditions hold, just a single set of repetitions of tensile and bending tests is to be performed on each material.
The details regarding the specific design of bending and tensile tests and the related results lie outside the description of the conceptual framework and will consequently be discussed separately.

3.1.4 Performance measurement

The subsequent step is the quantification of the response variables. A testing method is developed and validated, meaning it is ensured that the measurement is both accurate, differentiating among samples, and represents the phenomenon it is desired to describe.
Next, a design of experiment is developed to choose appropriately the combinations of key variables to study. Experiments are consequently performed.
The details regarding the specific design and the related results lie outside the description of the conceptual framework and will consequently be discussed separately.

3.1.5 Modelling & Prediction of performance

The development of a model correlating the identified key variables and the response variables can make use of a variety of techniques, from most simple regression methods in the case of a single scalar response to multivariate modelling techniques in the case of multiple non-independent predictors and responses (PCA and PLS are used in the specific instance).

In the case in which the predicted response variables are a curve or, more generally, multiple non-independent response variables are present, in order to deliver a more intuitive and readily accessible evaluation of the performance of the items under examination, it is recommended to identify one or more indices, which summarize the information regarding the performance of the item. The PCA methodology can be used for this purpose.

3.2 Denting Test Methodology

Having already identified the variables involved in the study, according to the conceptual framework, a screening experiment is to be performed. Clearly, in order to be able to assess the impact of a set of variables on a phenomenon, the phenomenon itself has to be measured. Hence the need for a methodology to quantify denting performance.

3.2.1 Test procedure

To measure the denting performance of a finished tube, cyclic force/deformation tests are performed on the items.

3.2.1.1 Room Conditions

The laboratory atmosphere is maintained in standard conditions: 23±2°C and 50±5% relative humidity.

3.2.1.2 Sample preparation

Depending on the aim of the specific experimental campaign, the tubes are prepared: each run of the campaign is characterized by a specific combination of values of the previously introduced variables; such values are ultimately fixed by choosing the material, the bulk fluid, the sealing conditions and technique, and the test ambient conditions.
The majority of such variables are thus determined during sample choice or during sample preparation; if the tubes to be tested are already filled and sealed, then follow the instructions o sample preparation from item number five; if the samples are available as empty, unfilled tubes, follow the whole procedure:

1. empty tubes of the **diameter** and **material** of choice are retrieved;

2. they are cut to the chosen **heights**;

3. they are **filled** up to the chosen levels;

4. they are **sealed** up in the chosen **conditions** (e.g. temperature), orientation and sealing tool;

5. a cross is drawn on the tube side, at 1/3 of the body height measuring from the end of the cap; in the case of laminate tubes, the cross should be on the opposite face with respect to the side seam.

6. the tubes are numbered to keep track of their "identity".

Note:
The filling operation is better performed using a scale, obtaining the weight of the mass of bulk to be introduced as the product of the desired volume and the density of the bulk.
The density of the bulk can be calculated with a sufficient degree of accuracy by measuring the weight of a liter of the bulk fluid.

3.2.1.3 Sample positioning and measurement

To perform the mechanical tests, the Zwick AllroundLine tester and the accessories introduced in Section 2.2.1.2 are employed.

The sample is fixed on the clamp (Figure 3.2), ensuring that the sealed back of the tube is properly fixed and that the pressing head position matches the cross drawn on the tube.

The logic of the cyclic force/deformation test is the following: at the beginning of each cycle the target imposed deformation is increased by a specified amount, starting from a value of 0mm before initiating the test; after the deformation reaches such value, the load is removed and the tube is allowed to return to its natural conformation, exerting a moderate force on the probe in the process. When the force exerted by the tube on the probe approaches zero, a measurement of the residual deformation of the tube is obtained and a new cycle begins; the process is repeated through numerous cycles.
At a certain value of imposed deformation, the corresponding residual deformation increases steeply; at this point, the tube has been dented. The cyclic test continues until the load reaches a threshold value.

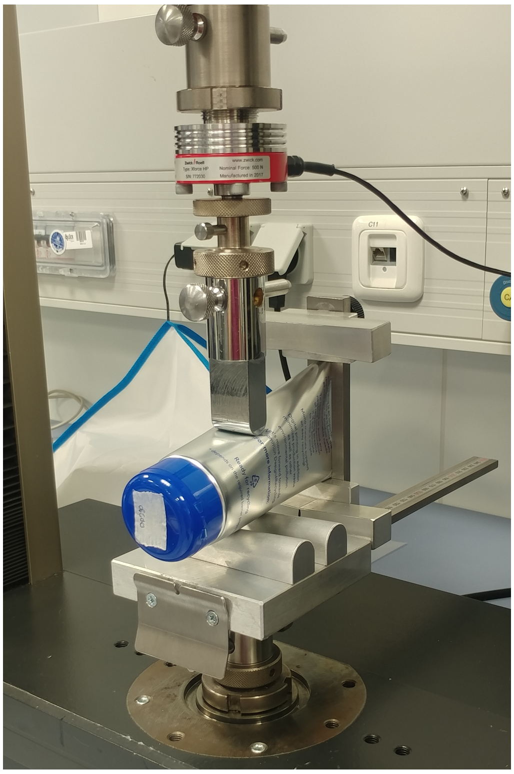


Figure 3.2. *Denting test setup.*

3.2.1.4 Zwick AllroundLine settings

A list of settings to implement this test methodology is here presented:

- pre-load:
  - force: 0.1N;
  - pre-load speed: 20mm/min;
  - no pre-load hold time;
  - time up to pre-load: 100s.
- cycles settings:
  - number of cycles: 50 (arbitrarily great amount, to ensure reaching threshold force)
  - first cycle target elongation: $1mm \cdot \frac{Tube\ diameter\ [mm]}{40mm}$;
  - increase in target elongation at each cycle: $1mm \cdot \frac{Tube\ diameter\ [mm]}{40mm}$;
  - hold time when reaching target deformation: 1s;
  - type of control in the load application phase of the cycle: position controlled;
  - load application phase speed: 1200 mm/min;

  - type of control in the load application phase of the cycle: position controlled;
  - load removal phase speed: 65 mm/min;
  - load removal force threshold (probe retraction accommodates sample movement): 0.1N;
  - hold time after reaching the threshold during load removal: 15s
  - the probe approaches pre-load (force of 0.1N) after each cycle;

- end of test: upper force limit of 40N; if denting doesn't occur with such force, the limit can be raised to 100N.

3.2.2 Test purpose and denting curves

Each test provides a great amount of information regarding the applied deformations and the corresponding forces; clearly, all this information needs to be summarized into a format which includes only the most relevant aspects for the scope of the experiment.
In this instance, the aspect of greatest interest is to identify the maximum deformation that a tube can accept without being permanently deformed (bounce-back behavior). The force applied to obtain such deformation is regarded as of secondary importance, considering that, during transportation and shelf life, the tube might be subject to a variety of stimuli of different magnitude, and ultimately what matters is that, within the range of motion of such stimuli, the tube is always capable to return to its original shape.

In this sense, the study of denting can be performed by focusing on the imposed deformation at each cycle and the related residual deformation after load removal. By fitting all such points (obtained from the series of cycles), a function correlating the two values can be obtained. Such curve will be referred to as "*denting curve*" (see Figure 3.3 for a conceptual scheme of the process).

It must also be addressed that both measures are better expressed in relative terms, dividing the deformations by the overall diameter of the tube under examination. The rescaled values thus represent the fraction of the tube that the probe has gone through; thus, relative deformations range from zero to one.
Interesting alternatives to this formulation of the denting curve exist: it is possible to study the imposed force or the imposed deformation energy (as the product of imposed force and deformation) on the abscissa (instead of the imposed deformation). These alternatives were not deemed appropriate for the case under study because, as explained, it is expected that the stimuli would be constrained by a range of motion more than by a maximum force or energy. Nonetheless, this is not generally valid, thus further studies might deem appropriate to change

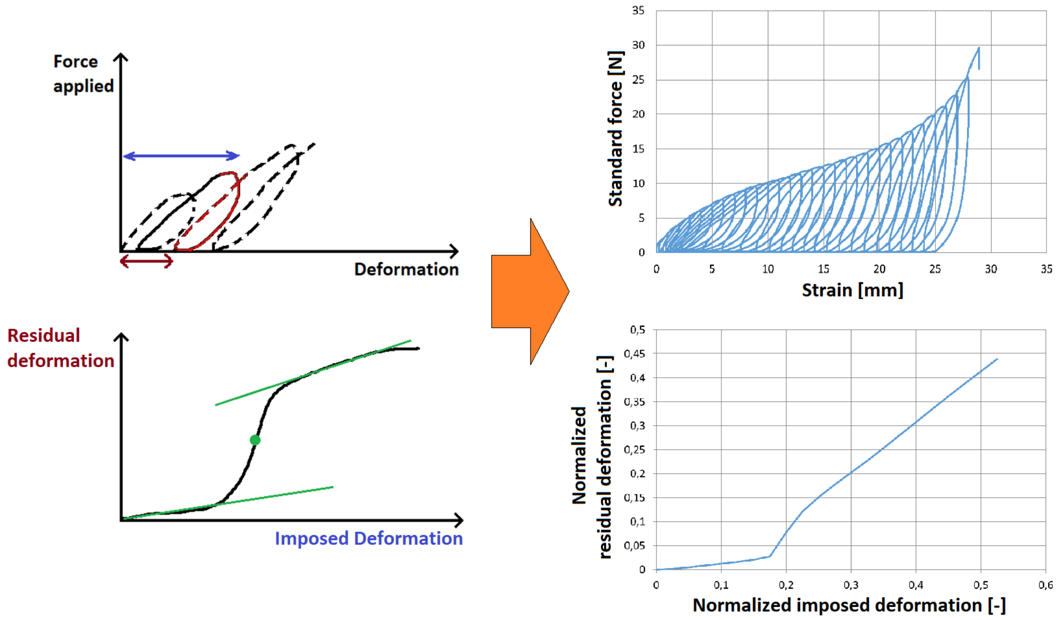


Figure 3.3. *First conceptual drawing of the denting curve and corresponding experimental results.*

the definition of denting curve depending on the specific needs.

Denting curves are a very important tool as they represent the response variable in the predictive model. Moreover, independently from model development, they can be:

- used as such, to quantitatively compare different tubes, both in terms of residual deformation upon small imposed deformation and to determine the conditions at which the dent arises;
- reworked to summarize the information in one or more denting indices; such an approach proves very effective to distinguish materials and characterize them in terms of denting performance; for this reason, the use of a denting index is deemed appropriate to provide an intuitive tool to compare tubes and will be discussed appropriately when introducing the modelling results in Section 3.6.1.

3.2.3 Method accuracy and validation

The NRMSE can be evaluated for each set of repetitions of the denting test, and provides information relatively to the variability of the measurements; moreover, considering that the normalization factor is common among all studied denting curves, this metric allows for a comparison among different denting tests, to better estimate the degree of accuracy of the methodology and to identify instances in which more repetitions are appropriate.
To quantify the accuracy of the method (capability to characterize each sample with sufficient accuracy to reliably differentiate among samples) and to validate it (showing that it fully captures the phenomenon of interest), measurements and a pretreatment script for the obtained raw

data are needed. For this reasons, conclusions regarding these topics are drawn in the following sections: for conclusions on method accuracy see Section 3.3.2.2 and for conclusions on method validation see Section 3.4.3.4.
For such reasons, the design of the experiments and the data management will have to be discussed before being able to draw conclusions regarding method accuracy and validation.

3.3 Scripts for automatic data management

Even though the experimental campaigns and their results have not been introduced yet, it was chosen to first present to the reader the data management methodologies, which only require the knowledge of the generic nature of the studied data. This allows for an easier presentation of the experimental campaigns in the following chapters, and for a clearer analysis of the resulting data.
Python algorithms have been developed into scripts to manage the raw data sourced from the testers, organizing them directly into Excel datasets.

The developed software, along with written instructions and a tutorial video series, was provided to the company. Data coming from any future experimental campaign will be readily treatable with such scripts, the outcome can then be fed into the JMP data analysis software files, either to perform predictions on new materials denting performance or to retrain the model.

3.3.1 Mechanical tests data pretreatment

The algorithms developed to perform the necessary treatments on the mechanical tests' raw data are here described. The data is first polished, meaning that it is transformed into a format which readily allows further manipulations, keeping only the relevant part. Consequently, the data is rearranged into a format which makes it possible to use it as dataset; two data management techniques were tried:

1. data alignment
2. curve fitting

Aligning the curves and using force/elongation values as predictors is a straightforward method that can lead to excellent models when combined with data analytics techniques capable of dealing with the high degree of collinearity (PLS for instance); unfortunately, aligning the data would have meant that some parts of the curves had to be cut out (see Figure 3.4), this would have implied a significant loss of data which was considered unacceptable. For this reason, the chosen strategy is to fit the curves and use the parameters of the fitting functions as predictors. This strategy, even if more complex (harder principal component interpretation and numerical complexity in fitting), allows to retain all data and ultimately results in a very general method and model.

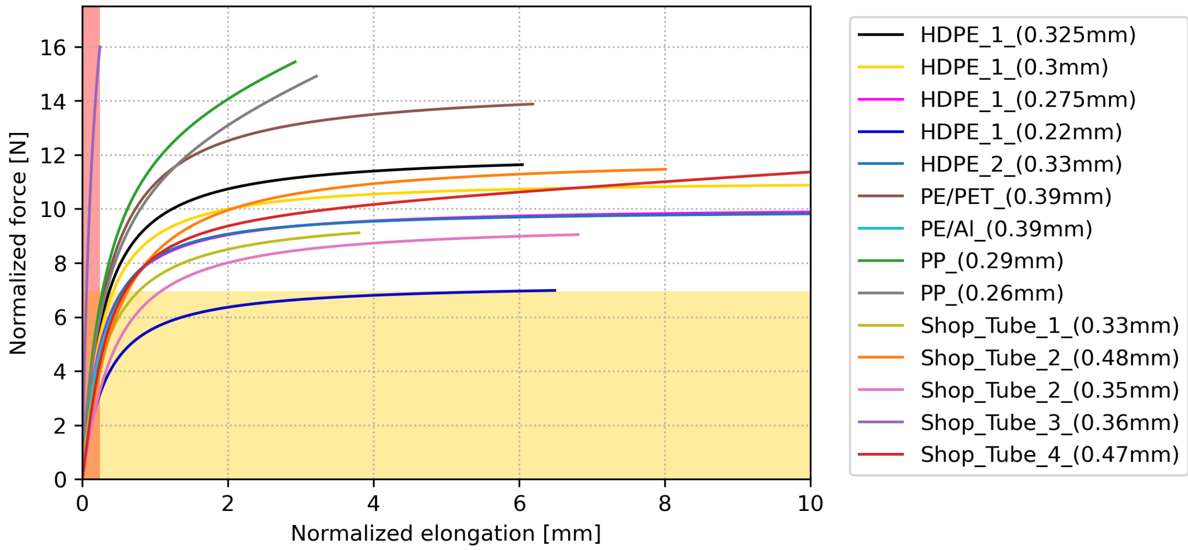


Figure 3.4. *Preview of the tensile test fitted curves, measured on 14 different materials. The red and gold areas show the portion of the data that could be used if alignment of the data points was performed to retrieve a dataset (respectively alignment along the x and y axis).*

3.3.1.1 Raw data clean-up

The algorithm for the clean-up of mechanical tests' raw data can be summarized in a series of key steps:

- data is collected from the raw data text files and organized in a Python dictionary according to test type, material, and repetition;
- out of all the raw data signals, only static force and position are kept and saved as vectors;
- static force and position vectors are shortened to contain only the data from the moment of the beginning of the test onward (from the moment at which a load is first applied);
- the position vector is transformed into an elongation vector by subtracting the first value of the vector from all its elements;
- due to small but noticeable differences in sample width and length, to be able to compare measurements, it is important to normalize the vectors with respect to a standard sample geometry; this geometry corresponds to a strip width and length of respectively 2 and 10mm:
  - in tensile tests, both forces and elongations need normalization; the forces are divided by the sample width [mm] and multiplied by 2mm; the elongations are divided by the sample length [mm] and multiplied by 10mm;

– in bending tests, due to the fact that in the three-point-bending test the sample length is naturally fixed to 10mm, only normalization of the forces is needed, by dividing the measurements by the sample width [mm] and multiplying by 2mm;

3.3.1.2 Data management and diagnostics

Broadly speaking, the extraction and enhancement of mechanical data from the raw test files is only the first step in the development of a dataset (to be used in model development): the data should be managed into a format on which the model can be trained and the quality of the data should also be verified.

Data alignment and averaging

The non-linear least square method can directly provide the best fitting function to a set of curves (repetitions of the experiment), thus the alignment and averaging of the repetitions is not a required step. Nonetheless, the procedure is here described because data alignment (among all curves, even across materials, and not just across repetitions) was tested as a first approach to building a dataset, and, apart from the problems described above, it would be a reliable technique. Thus, it is only reasonable to provide information regarding its implementation.
To align force-wise all the data and average the repetitions, the following procedure is implemented:

1. defining a unique, linearly-spaced vector of static forces, such vector must range from the pre-load value to the least among the maximum force values of all repetitions. The spacing among values must correspond to the average spacing between data points.

2. linearly interpolating the values of elongation for each test; linear interpolation is good in this instance, this can be proven by computing the maximum relative error due to interpolation through the following equation [3]:

$$e_r = \frac{(x-x_0)(x-x_1)}{2} \cdot \frac{f(x)''}{f(x_1)-f(x_0)} \tag{3.1}$$

where:

x = value to be linearly interpolated
x_0 = known value smaller than x
x_1 = known value greater than x
$e_r = \frac{f(x)-interp.\ value}{f(x_1)-f(x_0)}$
$f(x)$ = approximated function

In the studied cases, the values of the relative error always amount to a few percentage points, which is acceptable.

3. averaging, within each group of repetitions, the aligned values of elongation, to obtain a unique vector (repetitions-averaged elongation) for each test type and material; such vectors can be then stacked to generate a dataset of predictors.

Fitting functions derivation, parameters meaning and domain

The numerical methodology chosen to fit the data is the non-linear least squares method. Two different functions are chosen to fit the tensile ($f(x)$) and bending ($g(x)$) tests results:

$$f(x) = P1 \cdot \left(1 - \frac{1}{1 + (\frac{x}{P2})^{P3}}\right) \cdot e^{P4 \cdot x} \tag{3.2}$$

$$g(x) = P5 \cdot \left(\frac{1}{1 + e^{-P6 \cdot x}} - \frac{1}{2}\right) \tag{3.3}$$

Both functions are tuned to pass through the axes zero.

The Hill–Langmuir equation was originally formulated by Archibald Hill in 1910 to describe the sigmoidal O_2 binding curve of hemoglobin [10]:

$$\theta = \frac{1}{1 + \left(\frac{K_A}{[L]}\right)^n} \tag{3.4}$$

where:

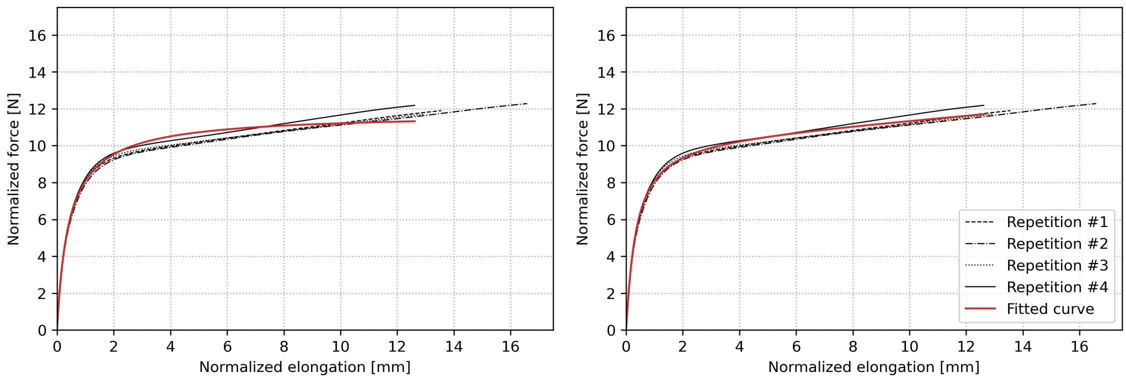
θ = is the fraction of the receptor protein concentration that is bound by the ligand;
K_A = is the ligand concentration producing half occupation;
$[L]$ = is the total ligand concentration;
n = is the Hill coefficient.

The equation then found broad application in a variety of fields as a modelling tool, commonly known as four parameters logistic curve (4PL).
$f(x)$ is obtained by modifying Hill's equation to better fit the data. Specifically, the plateau-like trend of the original function could not catch the deformation behavior of some polymeric materials when undergoing plastic deformations in tensile tests; thus, the introduction of an exponential factor granted the possibility to correct this fault and to obtain a function that, after the transition from elastic to plastic behavior, grows to infinity (still maintaining other important features of the original function, such as its origin).

To aid the method convergence, a series of constraints are imposed on the parameters, "shaping" the function coherently with the data trend; no particular initialization values are necessary and the initialization task can therefore be left to the software.

In the following list such constraints are described along with the mathematical meaning of the parameters; it is important to keep in mind that the function might be altered by the exponential contribution, making it harder to recognize the described effects of the parameters.

- $P1 > 0$: plateau value of the original Hill's function;
- $P2 > 0$: in the original Hill's function it determines the point of the curve whose value is $\frac{P1}{2}$; for $P3 > 1$ it also corresponds to the inflection point;
- $P3 > 0$: Hill's coefficient: it's a measure of the steepness of the curve; in the original Hill's function a markedly different behavior is observed for $0 < P3 < 1$ (concave function, P3 mostly affects the elbow of the curve) and for $P3 > 1$ (convex function up to P2, then concave);
- $P4 > 0$: coefficient of the exponential contribution; induces an upward trend on the function which helps to capture non-plateau-like behaviors.



(a) *Fitted with Hill's equation (4PL) - RRMSE between fit and measurements: 0.0175*

(b) *Fitted with modified Hill's equation (additional exponential factor) - RRMSE between fit and measurements: 0.0122*

Figure 3.5. *Tensile force/elongation curves of the material retrieved from "Shop Tube 2", fitted with different functions.*

The difference between a regression performed with the conventional Hill's function and with the modified one is displayed in Figure 3.5; even if the difference between the two curves appears slight, it is plausible that the upward asymptotic trend of some materials (not plateau-like) is associated to specific phenomena taking place during plastic deformation (e.g. necking, crystallization, strain hardening). Thus, having a parameter conceived with the whole purpose of capturing such behaviors (P4) has the potential to bring important benefits to the data-driven model.

$g(x)$ is a standard logistic function [8], where:

- $P5 > 0$: determines the plateau value (corresponds to twice its value);

- $P6 > 0$: represents the logistic growth rate (or steepness) of the curve.

Data quality and fit quality

The NRMSE between fit and measured values is chosen as a metric to evaluate the quality of the regression; the normalization factor is the maximum value of the fitted curve.
Even though the collected mechanical data has not been presented yet (Section 3.5.1), it can be anticipated that, for all fitted curves regarding mechanical data, the metric is always smaller than 6%, and on average is 2%.
This denotes that:

- the data variability is sufficiently small (thus also confirming that test method intrinsic variability and the chosen number of replicas are adequate);
- the chosen functions are adequate to capture the trend of the curves.

The choice of the NRMSE in place of the RRMSE is due to the fact that the latter is influenced by the average value of the curve, meaning that curves without a plastic plateau, having a lower average value, would present a significantly higher value of the RRMSE, even with an equally good fit.

Dataset formats

Having access to a reliable tool to fit mechanical tests data, it is now possible to discuss the available strategies to organize the dataset of the predictors:

- a first option could be to use the fitted functions to produce a set of aligned values of either imposed or residual deformations, differently from the direct alignment of the data discussed in Section 3.3.1, this option would not be inherently limited by the test with the least maximum elongation. Nevertheless, this option is disregarded because of the fact that, to avoid the excessive data loss comported by the alignment, extrapolation of the fitted functions would have to take place to an unreasonable degree; this would most surely lead to the generation of data which does not represent reality (see Figures 3.4 for a graphic representation of the issue);
- considering that each tested material is represented uniquely by the ensemble of the tensional and flexural coefficients, a second option is to concatenate such coefficients in a vector for each material; then, these vectors can be stacked to generate a dataset of predictors. In Table 3.2 a showcase of the predictors dataset structure is displayed.

3.3.2 Denting tests data pretreatment

The algorithms developed to perform the necessary treatments on the denting tests' raw data are here described. The data is polished and organized in a dataset in a similar manner to the procedure described for mechanical tests' results.

Table 3.2. *Showcase of the predictors dataset structure. P1, P2, P3, and P4 are the tensile data regression coefficients; P5 and P6 are the bending data regression coefficients.*

Material	Thickness	P1	P2	P3	P4	P5	P6
HDPE Lam. 1 - 325µmm							
HDPE Lam. 1 - 300µmm							
HDPE Lam. 1 - 275µmm							
HDPE Lam. 1 - 220µmm							
HDPE Lam. 2 - 330µmm							
PE/PET - 390µmm							
ABL - 390µmm							
PP - 290µmm							
PP - 260µmm							
Shop Tube 1 - 330µmm							
Shop Tube 2 - 480µmm							
Shop Tube 2 - 350µmm							
Shop Tube 3 - 360µmm							
Shop Tube 4 - 470µmm							

The data management techniques introduced in Section 3.3.1 (data alignment and curve fitting) are tested; in the end, simple alignment of the data proves inadequate, instead, good datasets can be built by first fitting the data and then either using the fitted parameter as they are, or generating aligned data (leveraging the curve fitting to avoid data losses). In the following subsections these strategies are discussed in greater detail.

3.3.2.1 Raw data clean-up

The key treatments performed by the algorithm on denting tests raw data are here described:

- raw data regarding each test (forces, corresponding deformations, corresponding cycle) is collected from the excel file and organized in a Python dictionary;
- auxiliary information, such as total number of tests and tube diameters is also extracted and saved;
- as described in Section 3.2, denting curves are derived only using a couple of points for each cycle of the denting test (imposed deformation and residual deformation); the imposed deformation is easily deduced for each cycle (based on the definition of the test, which is an imposed deformation test), meanwhile the residual deformation corresponds to the last value of deformation of the cycle;
- the imposed and residual deformation vectors are normalized with respect to the tube diameter; this allows to compare deformations among all tubes;

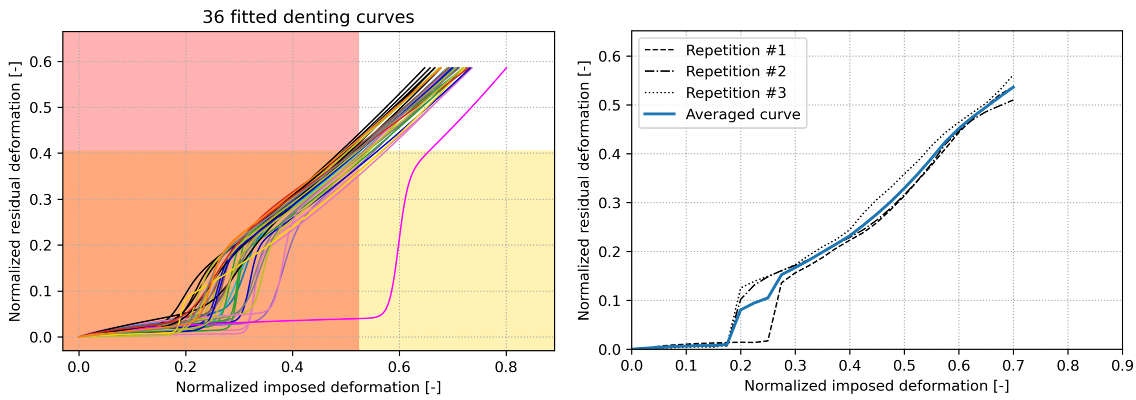
3.3.2.2 Data management and diagnostics

Exactly as for tensile and bending data, the extraction and enhancement of tensile data from the raw test files is only the first step in the development of a dataset (to be used in model development): the data should be managed into a format on which the model can be trained and the quality of the data should also be verified.

Data alignment, averaging and fitting

As discussed, to produce a dataset from a series of denting curves (comprehensive of repetitions), the most straightforward approach is to align all curves and to average the repetitions; in fact, the data is already aligned along the x axis thanks to the test design (imposed deformation test), but can also be reworked to be aligned along y axis. This doesn't require the effort of fitting the data and can lead to excellent models. Unfortunately, two problems were encountered when implementing this strategy:

- exactly as in the case of mechanical measurements, some data would have been excluded from the dataset (Figure 3.6(a)); only one curve would have been "cut" significantly, but such curve represents the best performing sample and thus losing part of its data was not acceptable.
- some of the repetition-averaged curves present anomalous behaviors, this happens in the cases in which the repetitions are noticeably dispersed and, in some cases, leads to a non-acceptable distortion of the resulting averaged curve (Figure 3.6(b)).



(a) *Preview of the denting fitted curves, measured on 36 different tubes. The red and gold areas show the portion of the data that could be used if alignment of the data points was performed to retrieve a dataset (respectively alignment along x and y axis).*

(b) *Example of anomaly that can occur in repetition-averaged denting curves (in the case in which repetitions are noticeably dispersed).*

Figure 3.6. *Illustrations of problems related to alignment and averaging applied to denting curves data.*

The solution to these issues is once again curve fitting.

Fitting the data with an appositely chosen function guarantees that the important features and shape of a denting curve are retained while using the data in their entirety and minimizing the distance from the sample points (least square method).
In this instance the task of identifying a function with the desired features is much harder, in fact, denting curves vary broadly under different aspects:

- initial slope;
- initial concavity;
- position of the inflection point;
- steepness at the inflection point;
- slope after the inflection point;
- concavity after the inflection point.

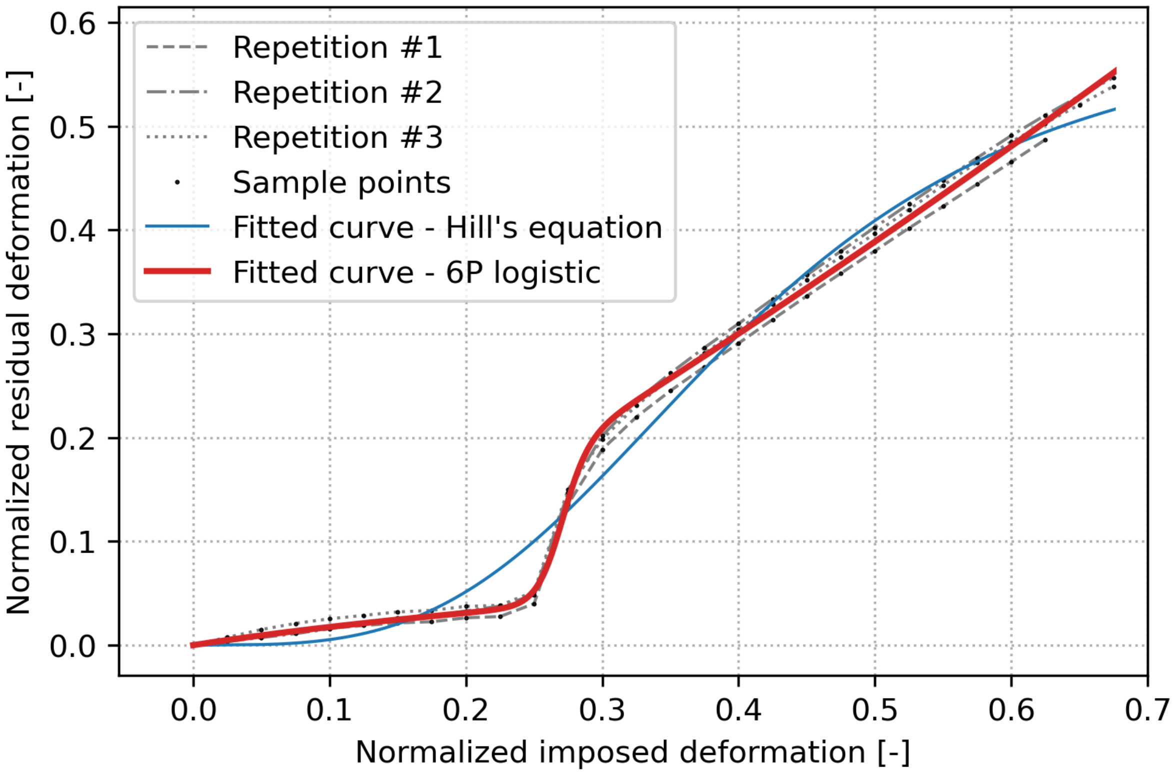


Figure 3.7. *Example of denting curve fitting. It is possible to observe the distinctive features described in Section 3.3.2.2; these features make it difficult to fit the data with conventional functions (Hill's equation for instance).*

The sigmoidal shape of the denting curve suggests that, for a first attempt, a logistic function could be used for fitting the data (Equation 3.3); unfortunately many characteristics of the logistic function are inadequate to fit the data:

- the symmetric nature of the logistic function proves inadequate for describing denting curves; in fact, such curves present a markedly different slope before and after the inflection point;
- the initial part of the denting curve is often convex, meanwhile the logistic function is concave;
- in denting curves, differently from logistic curves, no plateau-like trend is present for high values of imposed deformation.

The identification of a function capable of capturing all the features of the denting curves was a trial-and-error procedure, addressing step by step each of the above-described problems.
During the development of the fitting function for the tensile tests curves (Equation 3.2), it was observed that the absence of a plateau-like trend can be readily corrected by introducing a factor that grows to infinity, the idea is re-implemented here, with the factor x^{P8}; finally, the necessity for an initial slope and concavity was addressed by summing a logarithmic function ($P11 \cdot ln(P12 \cdot x + 1)$). After tweaking the structure of the equation and the initialization values of the parameters, the fitting proved rapid and reliable for all denting curves.

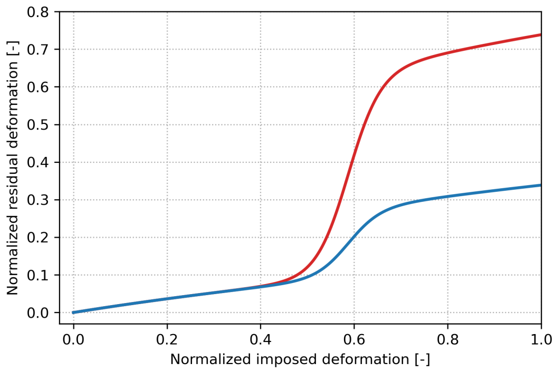
$$h(x) = \frac{P7 \cdot x^{P8}}{(1 + e^{-P10 \cdot x + P9})} + P11 \cdot ln(P12 \cdot x + 1) \tag{3.5}$$

<u>**Parameters initialization values and domain**</u>

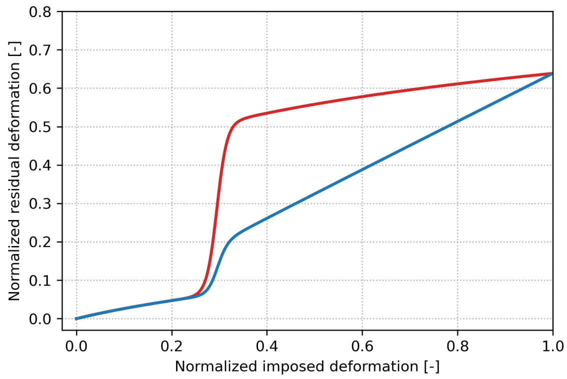
To help the non-linear least-square method converge, it is reasonable to restrict the domain of the parameters, this operation shapes the curve obtained from Equation 3.5, conferring it the desired features. Moreover, the set of initialization values for the parameters is equally relevant:

- $0 < P7 < 10$ / $P7_0 = 0.2$: scale factor, increases both the step height and the slope of the function (especially after the inflection point);
- $0 < P8 < 5$ / $P8_0 = 1$: determines the concavity of the function after the inflection point, also influences the height and the steepness of the step, but these last two features can then be altered independently by manipulating other parameters;
- $0 < P9 < 1000$ / $P9_0 = 20$: in conjunction with P10 determines position and steepness of the inflection point;
- $1 < P10 < 1000$ / $P10_0 = 50$;
- $0 < P11 < 3$ / $P11_0 = 0.1$: in conjunction with P12 determines the slope and the convexity of the curve before the inflection point, also has an impact on the slope of the curve after the inflection point, but this feature can then be altered independently by manipulating other parameters.

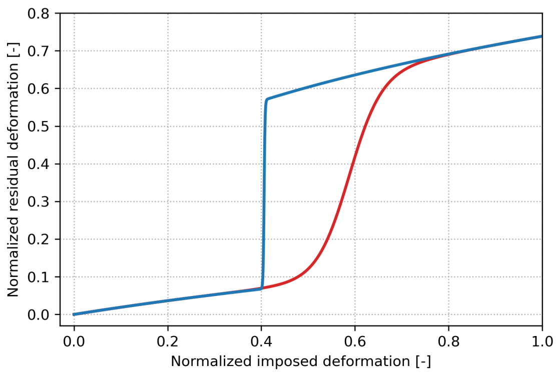
- $0 < P12 < 200$ / $P12_0 = 10$.



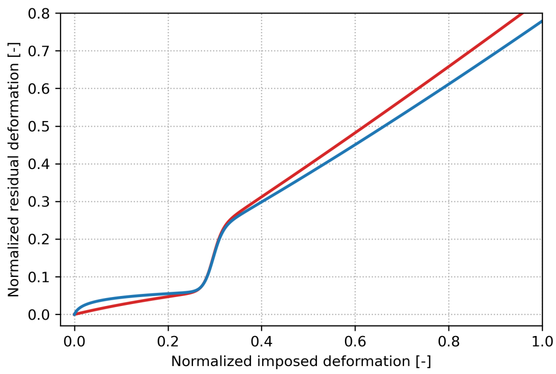
(a) *Display of the effect of parameter P7 on denting curves.*
Parameters settings: $P7_{Red} = 0.6$, $P7_{Blue} = 0.2$, $P8 = 0.2$, $P9 = 17$, $P10 = 29$, $P11 = 0.2$, $P12 = 1$.



(b) *Display of the effect of parameter P8 on denting curves.*
Parameters settings: $P7 = 0.5$, $P8_{Red} = 0.1$, $P8_{Blue} = 1.1$, $P9 = 28$, $P10 = 95$, $P11 = 0.1$, $P12 = 3$.



(c) *Display of the effect of parameters P9 and P10 on denting curves.*
Parameters settings: $P7 = 0.6$, $P8 = 0.2$, $P9_{Red} = 17$, $P9_{Blue} = 406$, $P10_{Red} = 29$, $P10_{Blue} = 1000$, $P11 = 0.2$, $P12 = 1$.



(d) *Display of the effect of parameters P11 and P12 on denting curves.*
Parameters settings: $P7 = 0.7$, $P8 = 1.2$, $P9 = 28$, $P10 = 95$, $P11_{Red} = 0.1$, $P11_{Blue} = 0.015$, $P12_{Red} = 3$, $P12_{Blue} = 192.8$.

Figure 3.8. *Display of the effect of the parameters on the Equation 3.5.*

Notice that:

- P7 and P8 mainly influence the section of the curve after the inflection point;
- P9 and P10 mainly influence features of the inflection point itself;
- P11 and P12 mainly influence the section of the curve before the inflection point.

Data quality and fit quality

The NRMSE between fit and measured values is chosen as a metric to evaluate the quality of the regression; the normalization factor corresponds to a normalized residual deformation of 0.6.

Even though the collected denting data has not been presented yet (Section 3.5.2), it can be anticipated that, for all fitted denting curves, the metric is always smaller than 3.5%, and on average it's 2%; this denotes that:

- the data variability is sufficiently small (thus also confirming that test method intrinsic variability and the chosen number of replicas are adequate);
- the chosen function is adequate to fit the curves.

The choice of the NRMSE in place of the RRMSE is due to two reasons:

- the NRMSE is a metric that allows comparisons between denting curves;
- the RRMSE is influenced by the average value of the curve, meaning that denting curves with a more pronounced initial elastic plateau would present a significantly higher value of the metric, even with an equally good fit.

<u>Dataset formats</u>

After acquiring a reliable tool to fit denting data, many options for building a dataset are available:

- using the inverse of the fitted functions to produce a set of aligned values of imposed deformation; meaning that a unique, linearly-spaced vector of residual deformations is chosen (common to all tests), then, for each test i, the corresponding vector of imposed deformation is evaluated as:

  $$[Imposed\ def.]_i = h_i^{-1}([Residual\ def.])$$

  Notice that:

  - the number of elements of the residual deformations vector should be in the hundreds, to guarantee an adequate description of all sections of the denting curves, independently of their slope;
  - depending on the range of the vector of residual deformations, this approach might lead to the extrapolation of some values (outside the original data range, see Figure 3.6(a)).

  The dataset is finally obtained by stacking the vectors $[Imposed\ def.]_i$.

- using the fitted functions to produce a set of aligned values of residual deformation; meaning that a unique, linearly-spaced vector of imposed deformations is chosen (common to all tests), then, for each test i, the corresponding vector of residual deformation is evaluated as:

  $$[Residual\ def.]_i = h_i([Imposed\ def.])$$

Notice that:

- the number of elements of the imposed deformations vector should be in the hundreds, to guarantee an adequate description of all sections of the denting curves, independently of their slope;
- depending on the range of the vector of imposed deformations, this approach might lead to the extrapolation of some values (outside the original data range, see Figure 3.6(a)).

The dataset is finally obtained by stacking the vectors $[Residual\ def.]_i$.

- The coefficients of the fitted denting curves represent them uniquely, thus contain, in a different form, the same variability of the denting curves. This means that the coefficients of each curve can be assembled in a vector and these vectors can be stacked to generate a response dataset.

All three strategies lead to datasets which contain in their entirety the relevant information initially present in the raw data; nonetheless, during predictive modelling, some of them might prove more prone than others to the extraction of such information. These topics will be discussed in detail in Section 3.5.3.

3.4 Key variables

Having introduced the concept of denting test and the algorithms used to transform the raw data into denting curves, it is now possible to implement these concepts to perform a screening test, identifying, among all variables that can possibly impact the denting performance, the most important ones (referred to as *key variables*).

3.4.1 Variables excluded a priori

Some of the variables introduced in Section 3.1.1 (see Table 3.1) are excluded a priori from the screening experiment, either because it has been already proven that they have a limited impact on denting (a priori knowledge), or because it was determined that they are less important than other variables for the aims of the project. In the latter cases, to guarantee the accuracy of the study, they cannot be simply disregarded; it should be ensured that their value is kept at a fixed value for the whole duration of the experiment. Moreover, these potentially impactful variables could be the focus of future in-depth studies.
Among excluded variables there is:

- **plastic or laminate:** all implications due to the production process of the material are caught in the data as differences in mechanical properties, with the exception of the macroscopic difference due to the presence/absence of the side seam. It is reasonable to assume that the denting performance is only marginally affected by this macroscopic feature of laminate tubes; it follows that the value of this variable can be regarded as influential and both kinds of tubes can be used indiscriminately for the tests;

- **internal pressure after sealing:** the effect of the sealing conditions and technique are non-negligible; however, the scope of the study was a comparative analysis among tubes, thus varying this variable was not of interest and the most convenient sealing conditions (lab ambient conditions) and technique (lab sealing machine) were adopted;

- **bulk fill level:** there are two reasons which could make the study of the fill level worth the effort; one is the fact that the amount of bulk fluid in a tube varies during use, and consequently denting propensity during use might increase; the other is that the fill level of the same product might vary regionally due to production necessities, and thus, if this variable were to be impactful, it might be responsible for regional worsenings of the denting performance.
  The first of the two aspects is not relevant in this study since it goes beyond the scope of the project, which mostly aims to assess the mechanical performance of the product during transportation and shelf life; the second aspect is instead of greater importance, nonetheless, it was chosen to not explore the impact of the fill level on denting, leaving the task to further studies on the topic.
  For the experiments here described, the fill level was kept constant at a common value (in Germany); this was achieved by scaling the volume of the bulk fluid to be introduced in a tube proportionally with respect to the tube height, using as reference the measure of bulk volume written on the print on existing finished products (see Table 3.3 and Figure 3.9).

Table 3.3. *Tube height and corresponding bulk fluid volume for common tubes in Germany.*

Tube height [cm]	Tube bulk fluid volume [ml]
D40	
0	0
15.5	150
17.5	160
D50	
0	0
17	220
20	275

- **vapor pressure:** the vapor pressure of the bulk fluid is only significantly different in presence of particularly volatile components (ethanol for instance); there are no components with such characteristics in conditioners and shampoos in sufficient amounts to entail

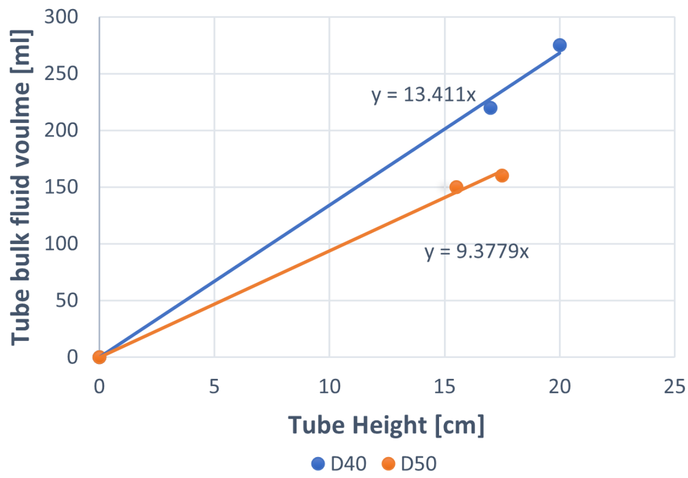


Figure 3.9. *Linear regression of common fill volumes for tubes in Germany as a function of tube height; allows to evaluate the volume of bulk fluid to be introduced in a tube of a certain height in order to guarantee a fixed fill level.*

an increase in tube internal pressure. Thus, the impact of component volatility on tube internal pressure and thus denting propensity was not evaluated.

- **chemical interactions among wall and bulk:** the impact of chemical interactions among tube wall and bulk is also not explored in this study; this is because sufficient care is taken by tube manufacturers in the material development to ensure that barrier layers prevent components from migrating from and into the tube wall. Thus, it is assumed that, in the time scale of the item life, the mechanical properties are unaltered as a consequence of the interaction with the bulk (as long as the bulk fluid introduced belongs to the family of products for which the tube was originally developed).

- **environmental conditions:** environmental conditions are very impactful on tube mechanical properties, so much so that they would deserve a study on their own. In fact, the great majority of all the studied variables is influenced to some degree by temperature. Pressure and ambient humidity impact the tube performance to a lesser degree, but still to non-negligible levels. Consequently, for the sake of focusing on tube performance differentiation among tubes, all three variables are fixed to standard laboratory conditions: (298.15K, 1atm, and humidity in between 30 and 50% relative humidity).

The impact of an additional factor is also studied in the test: accurately preparing samples is a material and labor-intensive procedure, thus it is of interest to understand whether denting tests can be performed multiple times on the same tube without significantly affecting the results. If this is not the case, multiple tubes should be prepared to perform replicas of the experiments. Such variable will be referred to as *repetitions on the same sample*.

3.4.2 Screening test design of experiment

The final set of studied variables (factors), and the corresponding levels are listed:

- **mechanical properties of the material:**
  two levels: HDPE Lam. 1 (300 µm) and ABL (390 µm);

- **tube diameter:**
  two levels: 40mm and 50mm;

- **tube height:**
  two levels: 17.5cm and 19cm;

- **dynamic viscosity of the bulk fluid:**
  two levels: tap water and conditioner;

- **repetitions on the same sample:**
  three levels: from new to two-times-tested tubes;

The two materials were chosen to be significantly different in thickness, composition, and perceived behavior, but also to allow all combinations suggested by the test design (for instance other materials are not available as tubes both in D40 and D50 format, or the tubes are not sufficiently high). If, as expected, the material choice has an impact on denting performance, it should thus be detected by the screening test.
The difference in tube body height is also significant (with respect to the common range of tube heights) and should thus be sufficient to detect any impact of the factor.

To facilitate the description of the experimental design let's make a distinction between the first four variables, which have only two levels, and the fifth (*repetitions on the same sample*), which has three levels. A factorial design is designated for each level of *repetitions on the same sample*:

- a full factorial design (2^4) is developed for non-tested tubes, namely testing each combination of diameter, height, bulk fluid and material;

- a 2^{4-1} factorial design is developed for the second and third round of tests performed on the tubes (see Figure 3.10).

A single replicate strategy is regarded as adequate for a screening experiment, also considering that the measure of denting curves is sufficiently accurate.
The regression model will only account for main effects and second-degree interactions.
The complete design is presented in Table 3.4.

Table 3.4. *Screening experimental design for assessment of factors influence on denting performance.*

Run	Repetitions on the same tube	Bulk fluid	Height of the tube [cm]	Diameter of the tube [cm]	Material
1	0	Tap Water	17.5	40	HDPE - 300µm
2	0	Tap Water	17.5	50	ABL - 390µm
3	0	Tap Water	19	40	ABL - 390µm
4	0	Conditioner	19	40	HDPE - 300µm
5	0	Conditioner	17.5	40	ABL - 390µm
6	0	Conditioner	19	50	ABL - 390µm
7	0	Tap Water	19	50	HDPE - 300µm
8	0	Conditioner	17.5	50	HDPE - 300µm
9	1	Tap Water	17.5	40	HDPE - 300µm
10	1	Tap Water	17.5	50	ABL - 390µm
11	1	Tap Water	19	40	ABL - 390µm
12	1	Conditioner	19	40	HDPE - 300µm
13	1	Conditioner	17.5	40	ABL - 390µm
14	1	Conditioner	19	50	ABL - 390µm
15	1	Tap Water	19	50	HDPE - 300µm
16	1	Conditioner	17.5	50	HDPE - 300µm
17	2	Tap Water	17.5	40	HDPE - 300µm
18	2	Tap Water	17.5	50	ABL - 390µm
19	2	Tap Water	19	40	ABL - 390µm
20	2	Conditioner	19	40	HDPE - 300µm
21	2	Conditioner	17.5	40	ABL - 390µm
22	2	Conditioner	19	50	ABL - 390µm
23	2	Tap Water	19	50	HDPE - 300µm
24	2	Conditioner	17.5	50	HDPE - 300µm
25	0	Tap Water	17.5	50	HDPE - 300µm
26	0	Tap Water	17.5	40	ABL - 390µm
27	0	Conditioner	17.5	40	HDPE - 300µm
28	0	Conditioner	17.5	50	ABL - 390µm
29	0	Tap Water	19	40	HDPE - 300µm
30	0	Tap Water	19	50	ABL - 390µm
31	0	Conditioner	19	50	HDPE - 300µm
32	0	Conditioner	19	40	ABL - 390µm

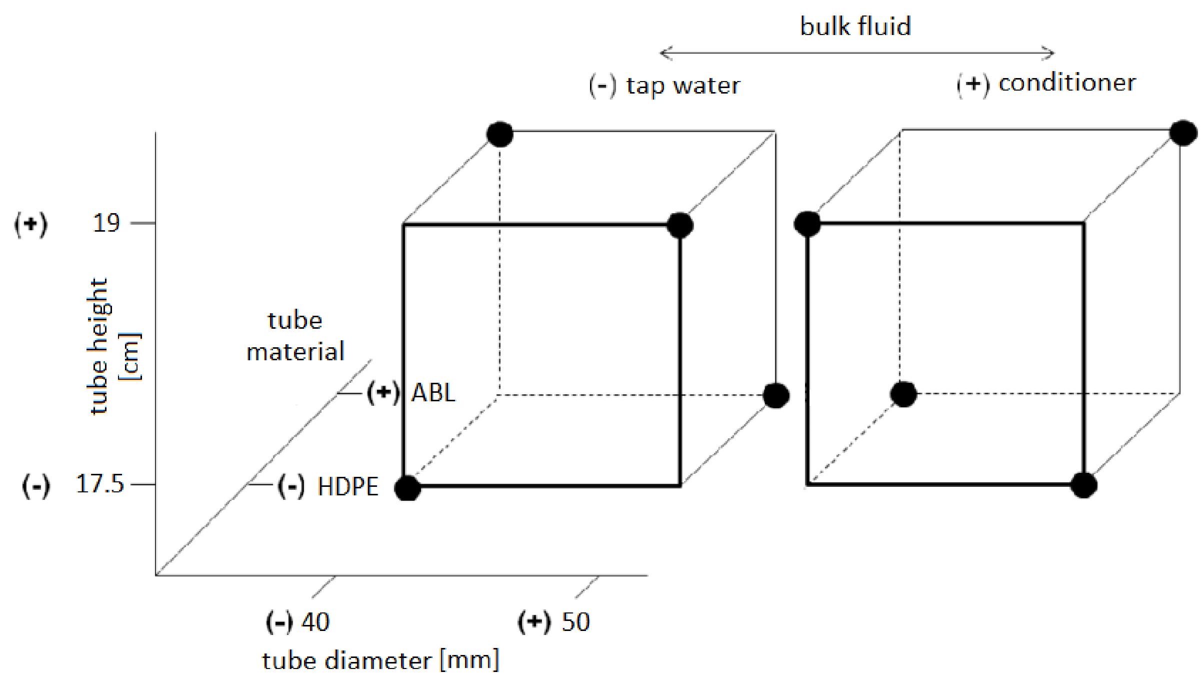


Figure 3.10. *Illustration of the* 2^{4-1} *factorial design developed for the second and third rounds of tests in the screening experiment.*

3.4.3 Screening test results analysis

The data obtained from the screening test don't need the complex pre-treatment described in the previous section. This is because:

- repetitions are not averaged, but studied independently to assess their impact, thus fitting single curves doesn't bring any benefit in terms of capturing the "mean trend", as in multiple curves;
- the denting curves of the two chosen materials develop fully within the same range of imposed deformations.

Thus, the values of residual deformation corresponding to each curve can be stacked to generate a dataset that is "naturally" aligned along the x axis (see Figure 3.11).

3.4.3.1 Performing a PCA on the denting test results

DoE methodologies have the purpose of identifying a statistically relevant set of experiments to study the effect of a group of independent variables (factors) on one or more responses; to get a clear picture of the factors' influence on the phenomenon under study, it is desirable that response variables are orthogonal.
This is not the case for the dataset obtained from the screening experiments; the response variables are not only not orthogonal, but even highly collinear in some cases.

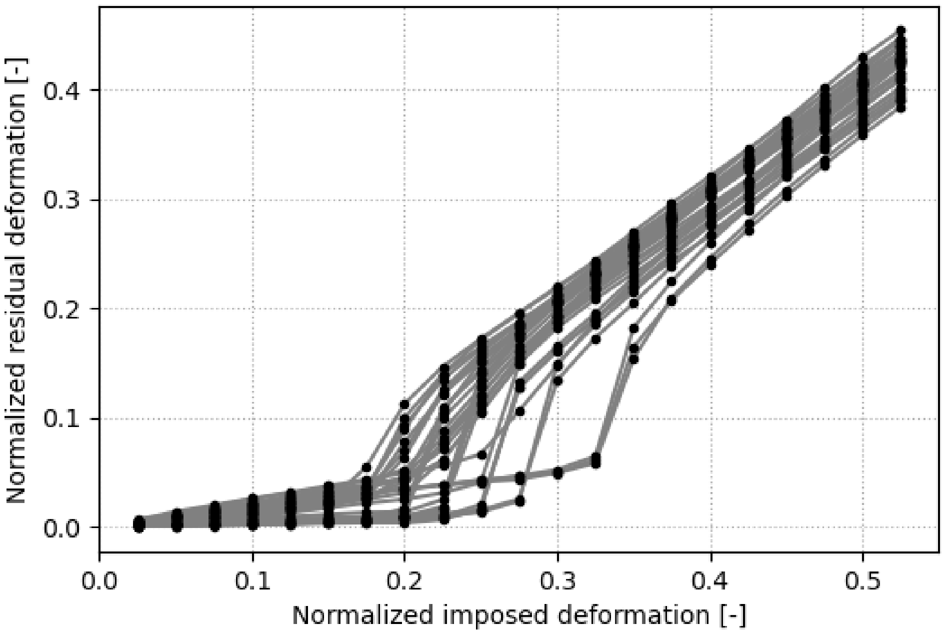


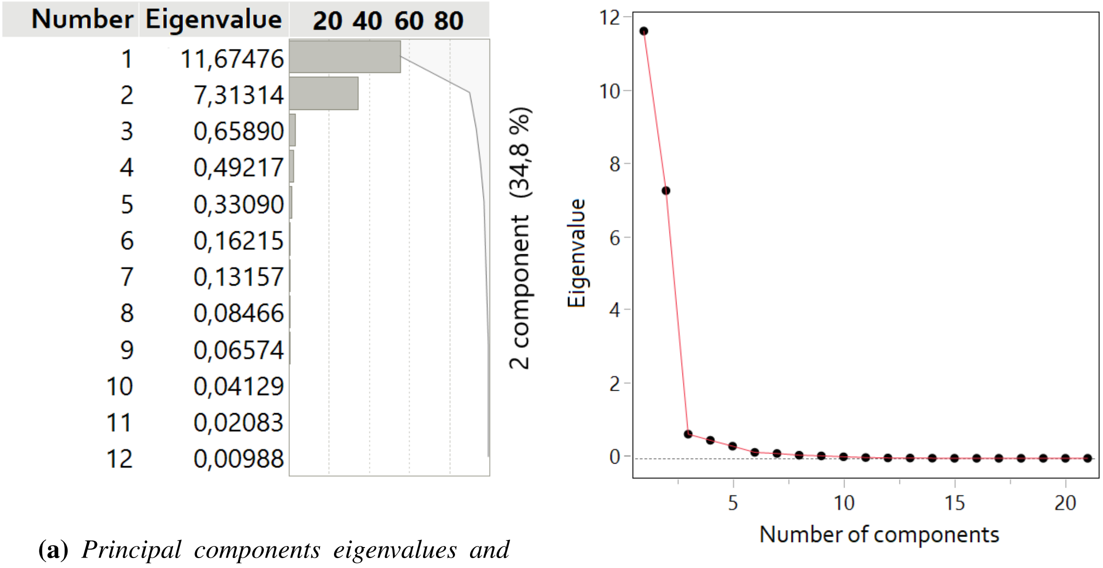
Figure 3.11. *Denting curves obtained from the 32 tests performed in the screening campaign; the dots display how the sample points are "naturally" aligned along certain values of imposed deformation.*

To reduce the response variables to a set of orthogonal ones, still maintaining the majority of the variability of the data, PCA is performed on the response dataset. The strategy of using the principal components of the response variables for estimating the unknown regression coefficients in a standard linear regression model is a technique often referred to as Principal Component Regression (PCR).

Both the cumulative captured variance plot (Figure 3.12(a)) and the scree plot [2] (Figure 3.12(b)) suggest that two principal components are sufficient to adequately describe the variability among the curves (over 90% of the curves variability is captured by the two first principal components).

The Hotelling's T^2 (Figure 3.13 above) statistic allows to assess the distance of the observation from the mean within the correlation structure identified by the model. The existence of outliers doesn't imply that the model is insufficient. It is simply needed to examine carefully these particular observations to ensure that their value is reliable, also considering that, given their distance from the model, they exert a strong influence. This is the case of measurements 4 and 12, which although outliers, as explained in the next paragraph, can be considered reliable thanks to a modest value of the Q statistic.

The Q statistic (Figure 3.13 below) allows to assess the distance of the observation from the hyperplane (correlation structure) of the model. In other terms, it quantifies the inability of the model to explain the variability associated with the measurement. A modest value of the Q statistic makes it reasonable to assume that an observation can be well explained by the model. A high value must instead be considered with care, because it means that the model, to some



(a) *Principal components eigenvalues and cumulative captured variance plot.*

(b) *Scree plot.*

Figure 3.12. *Metrics relative to the PCA performed on the dataset of denting curves retrieved from the screening tests.*

degree, is insufficient. Observations 2, 9, 18, and 26 are moderately over the upper confidence limit (with $\alpha = 0.05$); however, they are likely not measurement errors, but simply an indication that a 2 principal component model is incapable of fully explaining the behavior of some of the denting curves. Such observations can be kept in the dataset, considering that they have a moderate impact on the overall model (modest value of the T-squared statistic).

Score and loading plots are presented in Figure 3.14.
An attentive study of such plots helps to interpret the features of the denting curve captured by the two principal components: from the loading plot (Figure 3.14(f)) it can be inferred that the first principal component is mainly related to the terminal part of the curve (asymptotic section after the inflection point), meanwhile the second principal component is related to the first section of the denting curve (quasi-linear section before indentation); this helps us retrieving more information from the score plots:

- in Figure 3.14(a) it can be observed that the scores mainly differ among the two materials in terms of the second principal component; knowing that the second principal component is mainly relative to the initial part of the denting curve, and observing the corresponding denting curves, it emerges that the second principal component is mainly related to the initial slope of the denting curve (it is the main feature characterizing this part of the curves); the higher the value of the principal component, the higher the slope.

- in Figure 3.14(b) it can be observed that the scores mainly differ among the two diameter formats in terms of the first principal component; knowing that the first principal component is mainly relative to the asymptotic part of the denting curve, and observing the

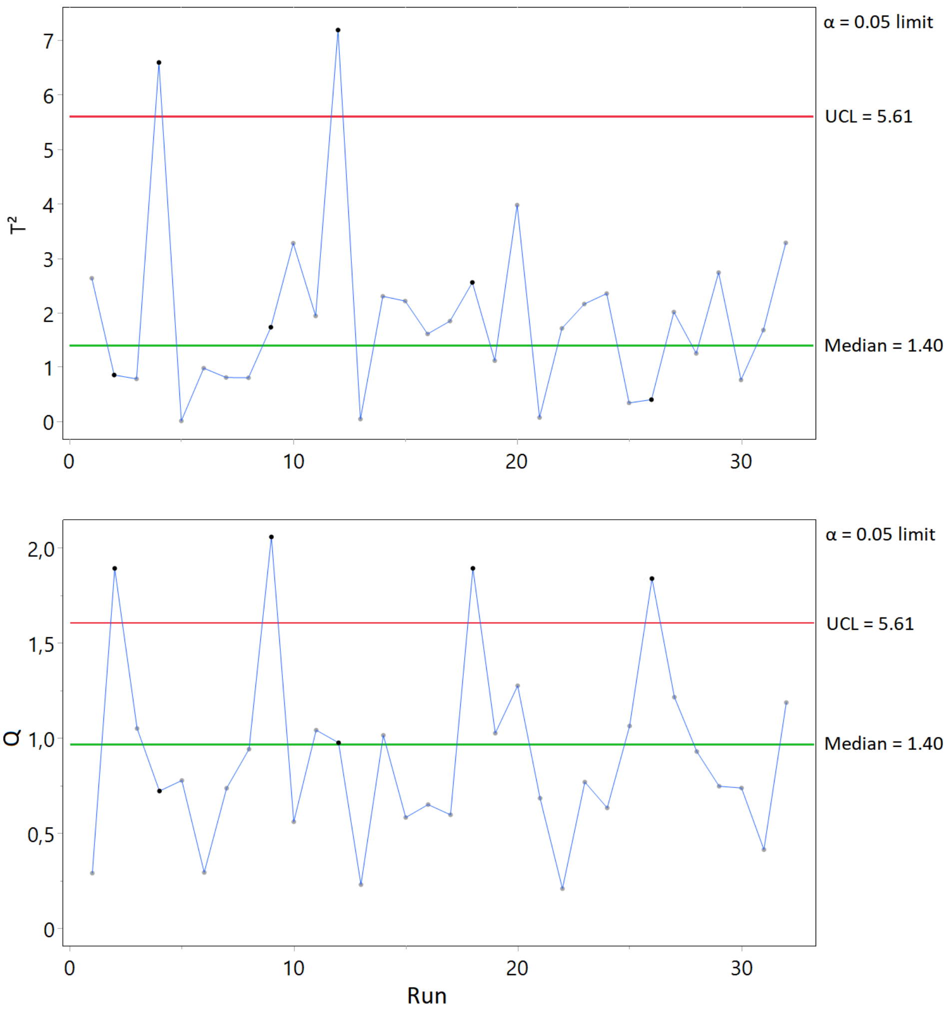


Figure 3.13. *T^2 and Q diagnostics relative to the PCA performed on the dataset of denting curves retrieved from the screening tests.*

corresponding denting curves, it emerges that the first principal component is mainly related to the value of the intercept of the asymptotes (it is the main feature characterizing this part of the curves); the higher the value of the principal component, the higher such intercept is.

Thanks to these observations, the principal components can be readily and reliably interpreted. If the effects of the studied factors didn't align so conveniently with the principal components, a more in-depth observation of the individual denting curves and corresponding scores would have proven necessary to arrive at a sound interpretation of the principal components.

Although Figure 3.14 already gave some insights on the influence that the factors might have on the principal components (and consequently on the denting curves), developing a regression model for the two principal components can provide a clearer picture regarding the relevance of each factor; this is the topic of the following section.

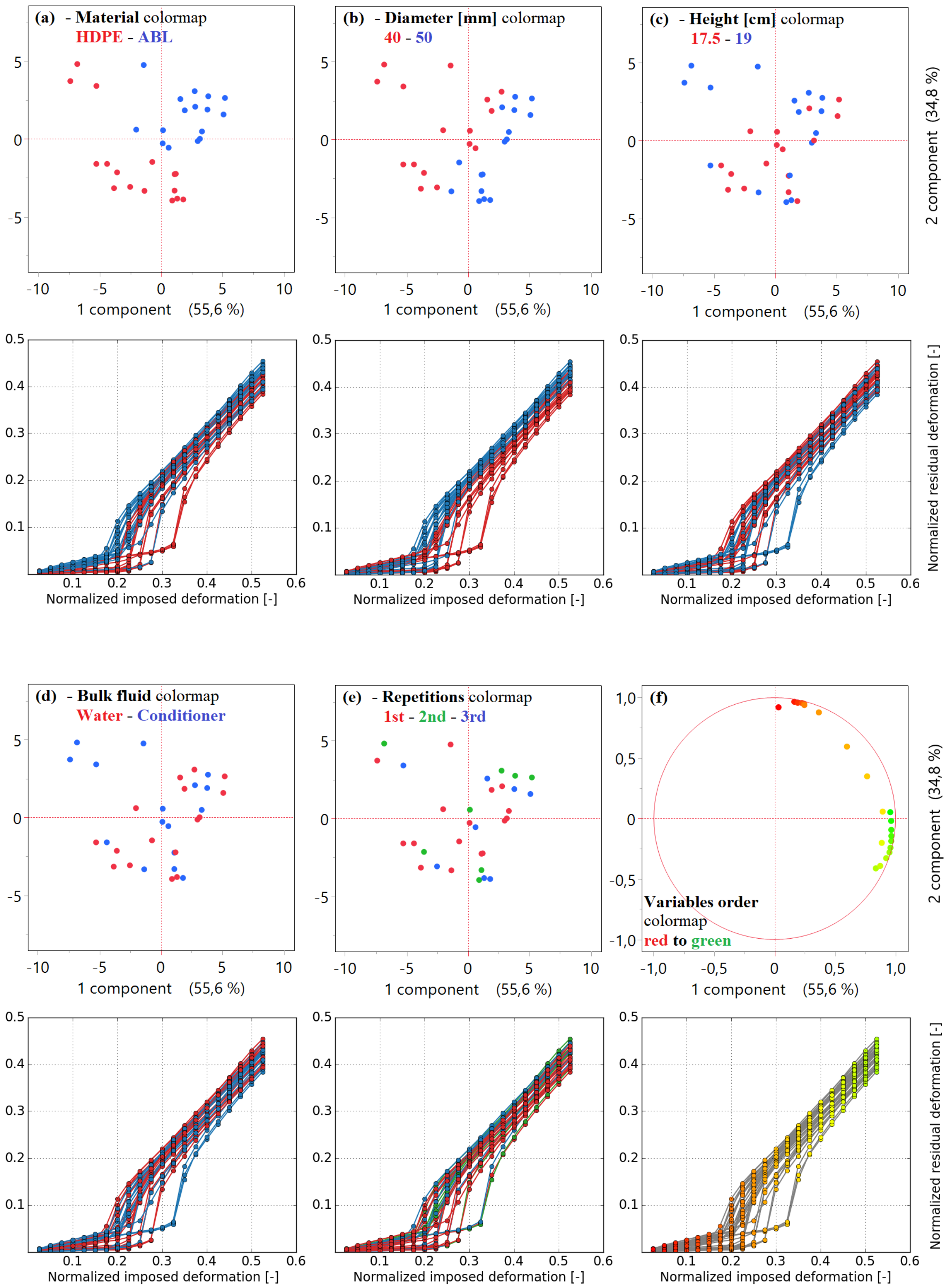


Figure 3.14. *Score and loading plots relative to the PCA performed on the screening tests' denting curves. The five score plots differ only for the color map, which displays the effect of each factor. The raw data curves, painted with the same color map, are juxtaposed.*

It is important to recall that, while a screening experiment can highlight the influence of the factors and their relevance, it doesn't include enough variety to develop a proper understanding of the underlying phenomena correlating predictors and responses; in other words, the only conclusion that will be drawn from the following analysis is the description of the effects that each factor has on the denting curve, but it will not allow to infer the reasons and mechanisms that lead to these correlations. This limit will be addressed with the development of a more complex model in Section 3.5.

3.4.3.2 Regression equation parameters and diagnostics

The multivariate least square method is implemented on the retrieved data; the fitting function is built accordingly to the test design, namely introducing main effects and second-degree interactions.

Two regression models are obtained, one for each principal component:

The parameters estimates for each of the two models are reported respectively in Table 3.5 and 3.6; the tables also report other metrics regarding factor relevance evaluation through hypothesis testing (Student's t-test).

Table 3.5. *Parameters estimates for PC1 obtained from the PCR performed on the screening denting tests data.*

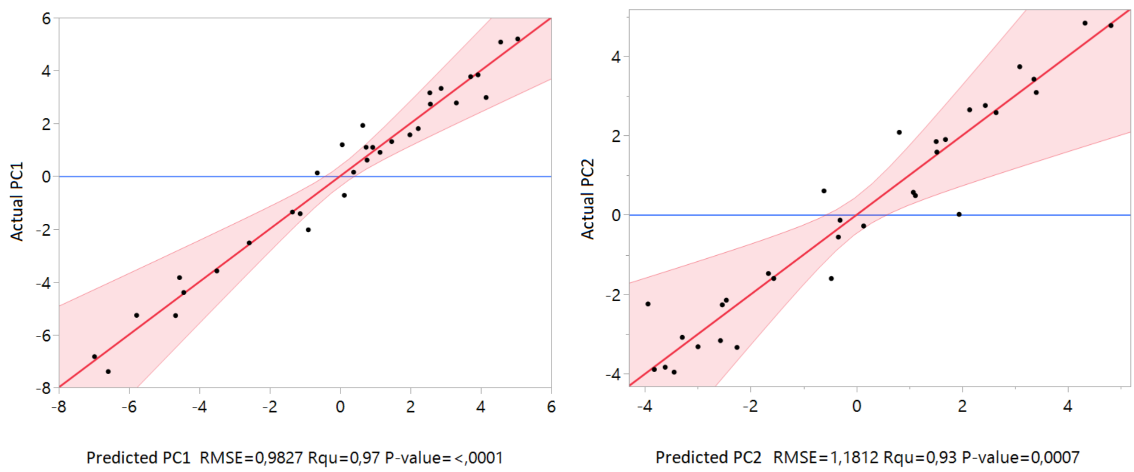
Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	0,2054365	0,183106	1,12	0,2858
Bulk[Water]	0,5764137	0,183106	3,15	0,0093*
Height(17,5,19)	-0,287456	0,183106	-1,57	0,1447
Diameter(40,50)	2,2305456	0,183106	12,18	<,0001*
Material[HDPE Lam. 1 - 300µm]	-2,159332	0,183106	-11,79	<,0001*
Bulk[Water]*Height	0,5084546	0,200583	2,53	0,0277*
Bulk[Water]*Diameter	-0,124878	0,200583	-0,62	0,5463
Bulk[Water]*Material[HDPE Lam. 1 - 300µm]	0,033804	0,200583	0,17	0,8692
Repetition on same tube[0]*Bulk[Water]	-0,286319	0,231613	-1,24	0,2421
Repetition on same tube[1]*Bulk[Water]	0,2979865	0,271591	1,10	0,2960
Repetition on same tube[0]*Height	0,150818	0,231613	0,65	0,5283
Repetition on same tube[1]*Height	0,0104367	0,271591	0,04	0,9700
Repetition on same tube[0]*Diameter	-0,057682	0,231613	-0,25	0,8079
Repetition on same tube[1]*Diameter	0,090445	0,271591	0,33	0,7454
Repetition on same tube[0]*Material[HDPE Lam. 1 - 300µm]	0,1875487	0,231613	0,81	0,4353
Repetition on same tube[1]*Material[HDPE Lam. 1 - 300µm]	-0,383534	0,271591	-1,41	0,1856
Height*Diameter	0,0131411	0,200583	0,07	0,9489
Height*Material[HDPE Lam. 1 - 300µm]	-0,41519	0,200583	-2,07	0,0628
Diameter*Material[HDPE Lam. 1 - 300µm]	0,307763	0,200583	1,53	0,1532
Repetition on same tube[0]	-0,821746	0,231613	-3,55	0,0046*
Repetition on same tube[1]	0,2327223	0,271591	0,86	0,4098

For each of the two models, the actual-by-predicted plot allows to evaluate the quality of the fit, which is considerably high, given the values of R^2 over 0.93 (Figures 3.15(a) and 3.15(b)).
Ultimately, in terms of diagnostics of the regression models:

- the absence of patterns or regularities in the plots of residuals against observation order and predicted value is checked (Figure 3.16(a-b) and 3.17(a-b)));

Table 3.6. *Parameters estimates for PC2 obtained from the PCR performed on the screening denting tests data.*

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	0,0533895	0,220095	0,24	0,8128
Bulk[Water]	-0,570842	0,220095	-2,59	0,0250*
Height(17,5,19)	0,9902542	0,220095	4,50	0,0009*
Diameter(40,50)	-0,849699	0,220095	-3,86	0,0027*
Material[HDPE Lam. 1 - 300µm]	-1,549895	0,220095	-7,04	<,0001*
Bulk[Water]*Height	-0,639185	0,241102	-2,65	0,0225*
Bulk[Water]*Diameter	0,4703343	0,241102	1,95	0,0770
Bulk[Water]*Material[HDPE Lam. 1 - 300µm]	-0,064637	0,241102	-0,27	0,7936
Repetition on same tube[0]*Bulk[Water]	-0,037513	0,278401	-0,13	0,8952
Repetition on same tube[1]*Bulk[Water]	-0,080204	0,326454	-0,25	0,8105
Repetition on same tube[0]*Height	-0,389962	0,278401	-1,40	0,1889
Repetition on same tube[1]*Height	0,12956	0,326454	0,40	0,6991
Repetition on same tube[0]*Diameter	0,1514154	0,278401	0,54	0,5974
Repetition on same tube[1]*Diameter	-0,176245	0,326454	-0,54	0,6000
Repetition on same tube[0]*Material[HDPE Lam. 1 - 300µm]	0,2164718	0,278401	0,78	0,4532
Repetition on same tube[1]*Material[HDPE Lam. 1 - 300µm]	-0,15551	0,326454	-0,48	0,6431
Height*Diameter	-1,093833	0,241102	-4,54	0,0008*
Height*Material[HDPE Lam. 1 - 300µm]	-0,006271	0,241102	-0,03	0,9797
Diameter*Material[HDPE Lam. 1 - 300µm]	-0,41228	0,241102	-1,71	0,1153
Repetition on same tube[0]	-0,213558	0,278401	-0,77	0,4592
Repetition on same tube[1]	0,5036307	0,326454	1,54	0,1512



(a) *Actual-by-predicted plot and fitting quality metrics regarding PC1 model.*

(b) *Actual-by-predicted plot and fitting quality metrics regarding PC2 model.*

Figure 3.15. *Actual-by-predicted plots regarding the PCR performed on the screening denting tests data.*

- the normality of standardized residual is checked (Figure 3.16(c) and 3.17(c)).

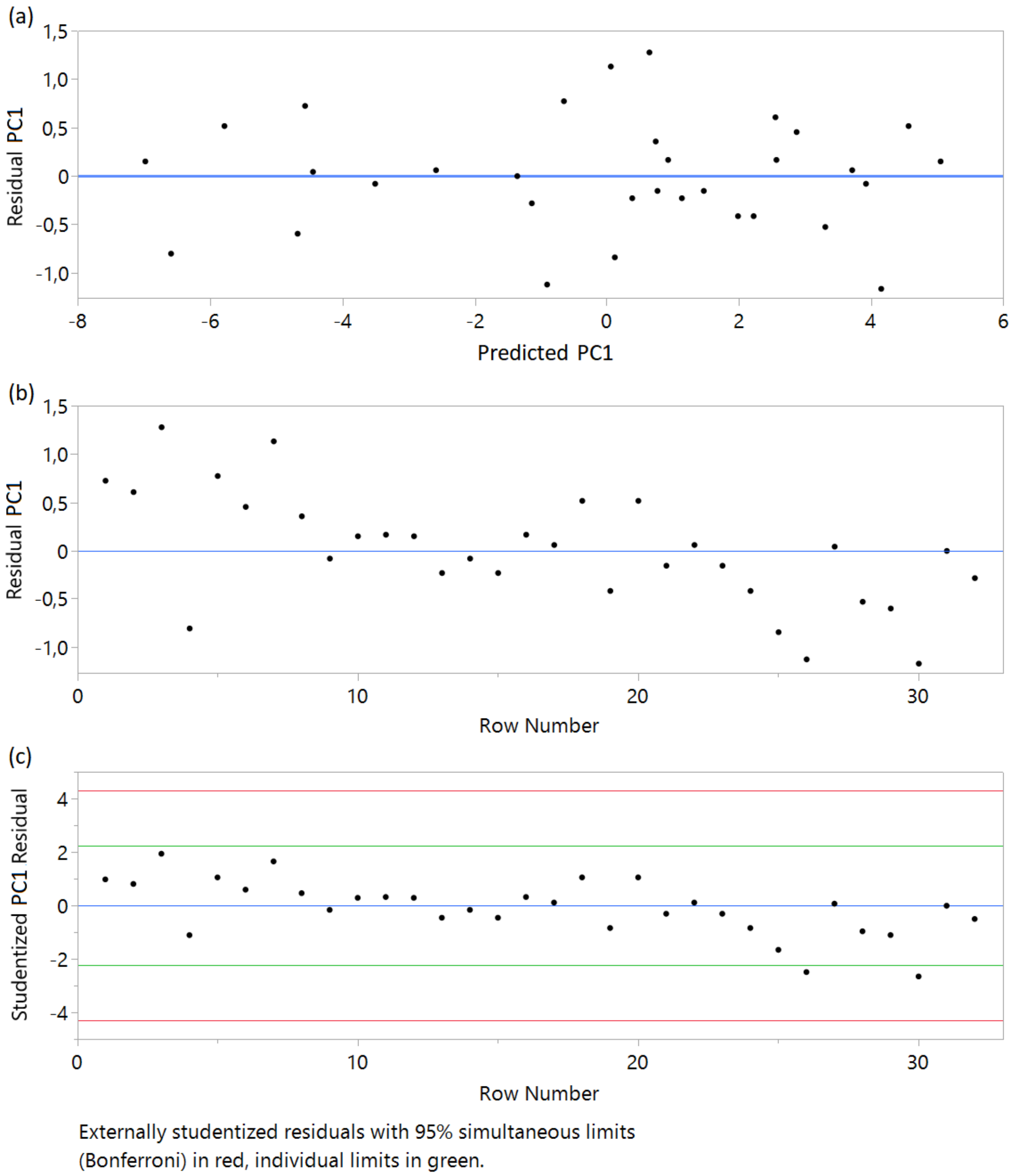


Figure 3.16. *Residuals of PC1 against predicted PC1 (a) and observation order (b); standardized residuals distribution (c). PCR performed on the screening denting tests data.*

The only abnormality observed is the downward trend of the plot in Figure 3.16(b); high positive values of PC1 residuals indicate that the model predicts on average lower values of the intercept of the denting curve's asymptote (with respect to the observed value), the opposite is true for high negative values. This is probably related to a poor tube-clamping technique in the preparation of the first tests. In fact, during the first tests, due to the limited familiarity

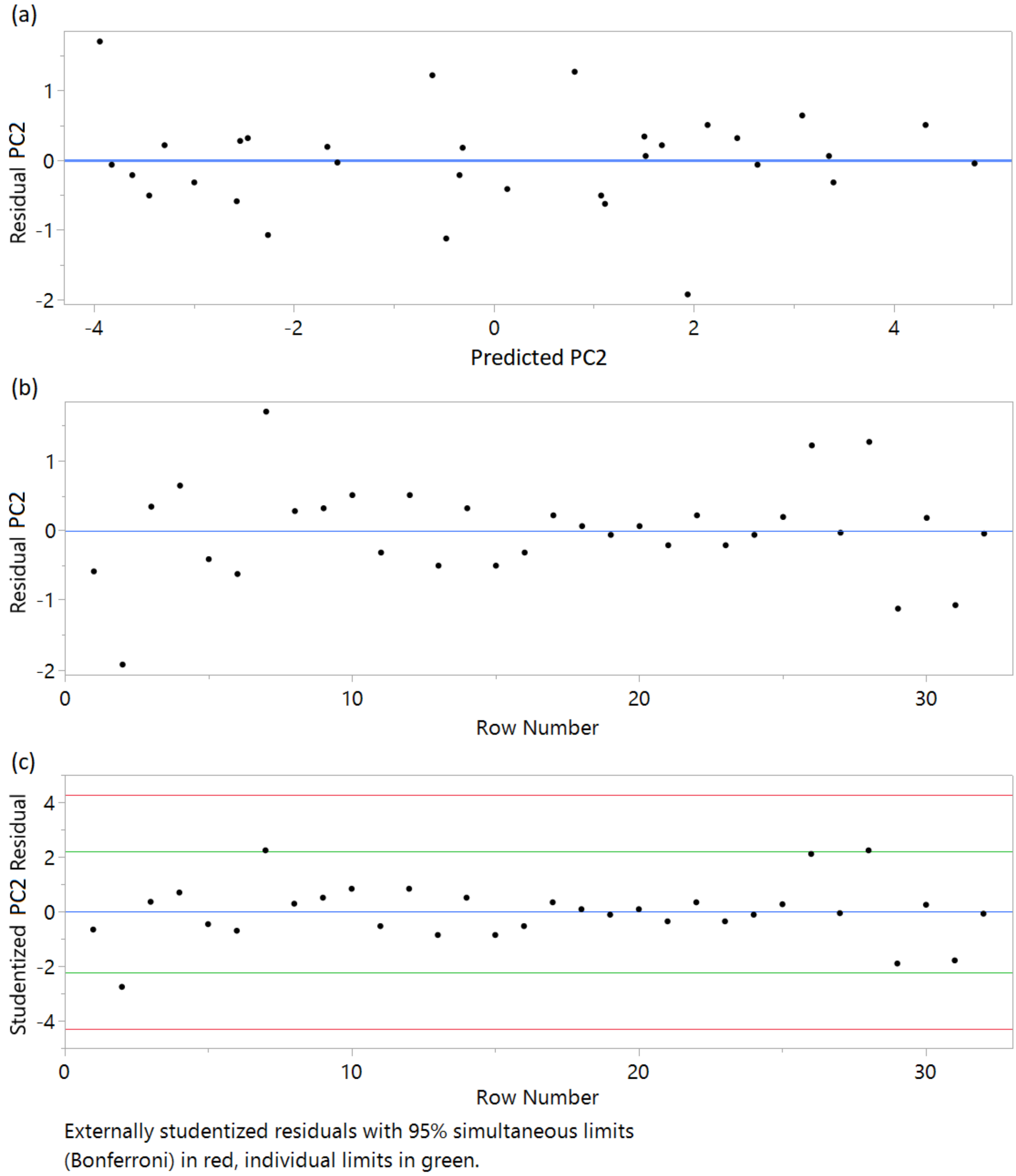


Figure 3.17. *Residuals of PC2 against predicted PC2 (a) and observation order (b); standardized residuals distribution (c). PCR performed on the screening denting tests data.*

with the device, the clamping strength exerted on the tubes was not sufficient, leaving room for the tube to slightly slip, thus introducing an experimental error in terms of residual deformation.

This highlights the importance of careful experiment preparation, in particular, of an adequate tube clamping in denting tests, capable of resisting tens of newtons of applied force.
Nonetheless, the introduced error is slight, and it can be assumed that it won't affect signifi-

cantly the results of the test, especially considering its screening purpose.

3.4.3.3 Influence of the factors

Having verified the reliability of the screening test regression model, it is possible to draw conclusions regarding the influence of each factor on the principal components and their relevance to the model.

From Table 3.7 it results that all 5 factors are statistically relevant for the model. This means that removing any factor will inevitably worsen the model.

Table 3.7. *P-values summary table of the PCR performed on the screening denting tests data. For each effect, the smallest p-value is reported (between the two principal components regression models). The blue line represents the 0.05 threshold limit, over which the null hypothesis is rejected (removing the effect the fit worsens significantly on a statistical level). The "logworth" represents the opposite of the logarithm (base 10) of the p-value.*

Source	Logworth	PValue
Diameter(40,50)	7,001	0,00000
Material	6,857	0,00000
Height*Diameter	3,071	0,00085
Height(17,5,19)	3,045	0,00090 ^
Bulk	2,033	0,00928
Repetition on same tube	1,875	0,01334
Bulk*Height	1,647	0,02254
Height*Material	1,202	0,06278
Bulk*Diameter	1,113	0,07702
Diameter*Material	0,938	0,11529
Repetition on same tube*Material	0,408	0,39117
Repetition on same tube*Height	0,401	0,39713
Repetition on same tube*Bulk	0,385	0,41183
Bulk*Material	0,100	0,79359
Repetition on same tube*Diameter	0,088	0,81701

The main effect trends of the five factors (Figure 3.18) match the expectations, namely:

- principal component 1, representing the intercept of the denting curve asymptote, is larger for ABL tubes, and also increases for greater tube diameters, heights, and with repetitions on the same sample. Its value increasing is related to an "earlier" denting of the tube in terms of imposed deformation. In these regards the model matches expectations;

- principal component 2, representing the initial slope of the denting curve, is larger for ABL tubes, also increasing for greater tube heights, and diameters; this means that larger and stiffer tubes tend to retain small imposed deformations to a greater degree (the word "stiffer" is a generalization, see Section 3.5.4 to better understand the impact of material properties). Also in these regards, the model matches expectations;

- the main effect of *bulk* on both principal components is modest;

- the main effect of *repetitions on the same tube* on principal component 2 is modest; this can be explained considering that the defects produced on the tube wall by previous repetitions mostly influence the last part of the denting curve, where the indentation is forming, while they do not alter significantly the first part of the denting curve, which is mainly determined by the capability of a tube to accommodate small imposed deformations.

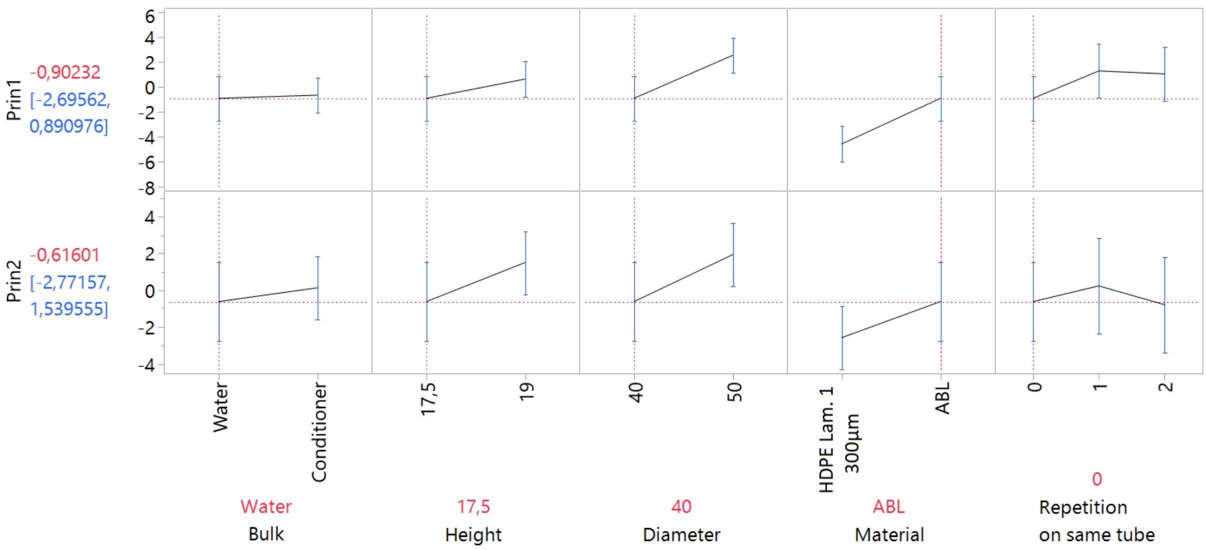


Figure 3.18. *Main effects plots for both principal components regression models. PCR performed on the screening denting tests data.*

The factors *repetitions on the same tube* and *bulk*, even though non-negligible, are less impacting than the others. Let's now recall that one of the original reasons for the design of a screening test was the assessment of the influence on the denting curves of test repetitions on the same tube. Specifically, it was desired to evaluate whether repetitions altered the behavior of a tube dramatically, to the point of not being able to use repeated measurements on the same tube as replicas of the experiment, or whether repetitions, although including some noise, still provide denting curves resembling the ones of non-tested tubes.

In this regard, it is unimportant that including the effect *repetitions on the same tube* statistically grants a better model. What's relevant is whether the model obtained without such effect is still good or not, even if certainly worse than the starting one.
This can be readily assessed by adjusting the model equation (and parameters) not to include the *repetition on the same tube* factor. This automatically means treating the different repetitions of the test performed on the same tube as replicas of the experiment. From the analysis of the model's quality, it is possible to assess the viability of the strategy.

The remaining factors' p-values (Figure 3.8) and the related main-effects plots (Figure 3.19) are not altered significantly.
But the most important indicator that the model remains adequate, and that replicas can be performed on the same sample (still obtaining a good explanatory capability of the denting phenomenon) is provided by the actual-by-predicted plots (Figures 3.20(a) and 3.20(b)). In fact,

Table 3.8. *P-values summary table of the PCR performed on the screening denting tests data excluding the effect "repetitions on the same tube". For each effect, the smallest p-value is reported (between the two principal components regression models). The blue line represents the 0.05 threshold limit, over which the null hypothesis is rejected (removing the effect the fit worsens significantly on a statistical level). The "logworth" represents the opposite of the logarithm (base 10) of the p-value.*

Source	Logworth	PValue
Diameter(40,50)	9,379	0,00000
Material	9,007	0,00000
Height*Diameter	4,331	0,00005
Height(17,5,19)	4,029	0,00009 ^
Bulk	2,293	0,00509
Bulk*Height	2,150	0,00708
Bulk*Diameter	1,403	0,03950
Diameter*Material	1,168	0,06794
Height*Material	1,039	0,09144
Bulk*Material	0,116	0,76582

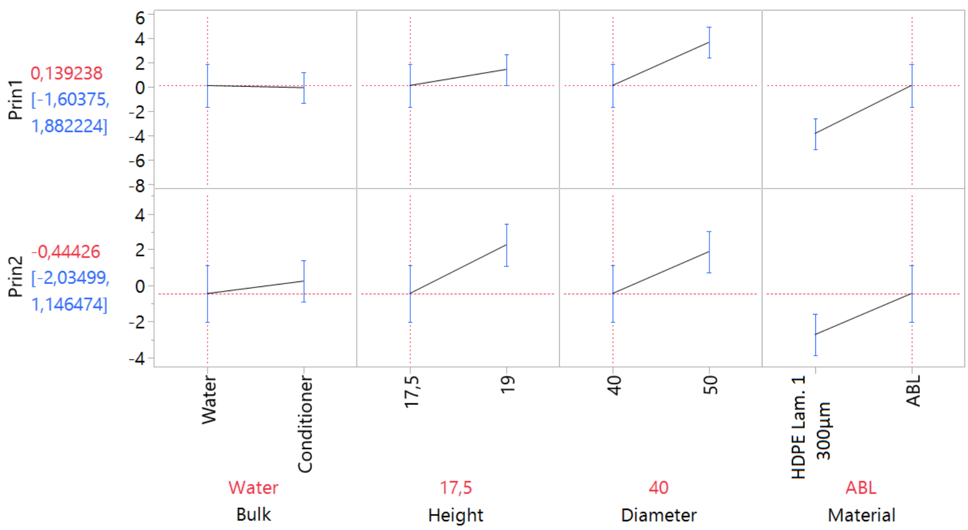
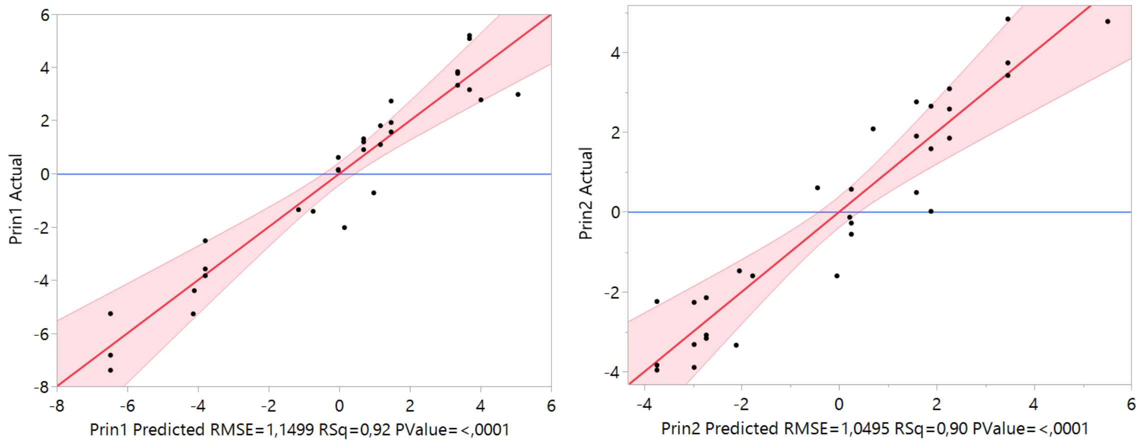


Figure 3.19. *Main effects plots for both principal components regression models. PCR performed on the screening denting tests data excluding the effect "repetitions on the same tube".*

the R^2 remains over 0.90 for the new regression models of both principal components.

The additional variability introduced in the model by this approach is the consequence of a variation in the mechanical structure of the tube after each repetition; this variation is due to the generation of defects on the tube wall.
An additional benefit of performing replicas on the same sample is that such defects might be also "naturally" present in real applications, rendering the averaged denting behavior obtained by performing replicas on a single tube more representative of the real phenomenon (happening for instance in tube transportation) than what would be measured by performing replicas on newly prepared tubes.



(a) *Actual-by-predicted plot and fitting quality metrics regarding PC1 model.*

(b) *Actual-by-predicted plot and fitting quality metrics regarding PC2 model.*

Figure 3.20. *Actual-by-predicted plots regarding the PCR performed on the screening denting tests data excluding the effect "repetitions on the same tube".*

All these considerations lead to the conclusion that replicas of the experiments can be performed on the same tube and that the factor *repetitions on the same tube* can be neglected.

Discussing the relevance of the *bulk* factor is also important: the tested fluids are broadly different in terms of dynamic viscosity, this was done on purpose to properly study the impact of the factor. The results showed that the factor is barely statistically significant with the studied levels; it is thus expected that switching from one conditioner to another would lead to an even less perceptible change in the denting curves, very likely a non-statistically relevant one. This is supported by the orders of magnitude of difference between water viscosity (1 cP) and cosmetic products viscosity (ranging in the thousands of centipoises [22]).

Tables 3.9 and 3.10 contain the parameters of the PCR models developed on the screening denting tests data excluding the effect "repetitions on the same tube" (reported for completeness).

3.4.3.4 Conclusions regarding denting test method validation

Other than proving model reliability, the above analysis also allows to finally draw conclusions regarding the validation of the denting test method: given that the observations regarding the statistical influence of the factors on the denting curves match expectations, it can be concluded that the testing methodology is in itself capable of capturing and quantifying the phenomenon of tube indentation.

Table 3.9. *Parameters estimates for PC2 obtained from the PCR performed on the screening denting tests data excluding the effect "repetitions on the same tube".*

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	-4,56e-14	0,203276	-0,00	1,0000
Bulk[Water]	0,5048339	0,203276	2,48	0,0215*
Height(17,5,19)	-0,249751	0,203276	-1,23	0,2328
Diameter(40,50)	2,2161252	0,203276	10,90	<,0001*
Material[HDPE Lam. 1 - 300µm]	-2,112445	0,203276	-10,39	<,0001*
Bulk[Water]*Height	0,5084546	0,234723	2,17	0,0420*
Bulk[Water]*Diameter	-0,124878	0,234723	-0,53	0,6003
Bulk[Water]*Material[HDPE Lam. 1 - 300µm]	0,033804	0,234723	0,14	0,8869
Height*Diameter	0,0131411	0,234723	0,06	0,9559
Height*Material[HDPE Lam. 1 - 300µm]	-0,41519	0,234723	-1,77	0,0914
Diameter*Material[HDPE Lam. 1 - 300µm]	0,307763	0,234723	1,31	0,2040

Table 3.10. *Parameters estimates for PC2 obtained from the PCR performed on the screening denting tests data excluding the effect "repetitions on the same tube".*

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	3,303e-15	0,18552	0,00	1,0000
Bulk[Water]	-0,58022	0,18552	-3,13	0,0051*
Height(17,5,19)	0,8927637	0,18552	4,81	<,0001*
Diameter(40,50)	-0,811845	0,18552	-4,38	0,0003*
Material[HDPE Lam. 1 - 300µm]	-1,495777	0,18552	-8,06	<,0001*
Bulk[Water]*Height	-0,639185	0,21422	-2,98	0,0071*
Bulk[Water]*Diameter	0,4703343	0,21422	2,20	0,0395*
Bulk[Water]*Material[HDPE Lam. 1 - 300µm]	-0,064637	0,21422	-0,30	0,7658
Height*Diameter	-1,093833	0,21422	-5,11	<,0001*
Height*Material[HDPE Lam. 1 - 300µm]	-0,006271	0,21422	-0,03	0,9769
Diameter*Material[HDPE Lam. 1 - 300µm]	-0,41228	0,21422	-1,92	0,0679

3.5 Predictive model for denting performance

Let's summarize the achievements presented so far:

- a test methodology to quantify tube denting performance has been developed and validated;
- a set of key variables, responsible for the difference in denting performance among products in the market, has been identified;
- the scripts for data management and quality evaluation have been developed.

Leveraging these results, it is possible to describe the experimental campaigns to retrieve data for model development:

- an experimental campaign is performed to collect mechanical data regarding all available materials (Section 2.1.1), according to the methods presented in Section 2.3.3 and 2.3.4.1;

- an experimental campaign is performed to collect the denting data regarding tubes composed of the above-mentioned materials, with geometries varying both in terms of height and diameter.

The data, once collected and organized into datasets (through the algorithms discussed in Section 3.3), is used to develop a predictive model, correlating macroscopic features of the tube and mechanical properties of the constituent material (predictors) with denting performance (responses). In Figure 3.21 a schematic representation of the process is displayed.

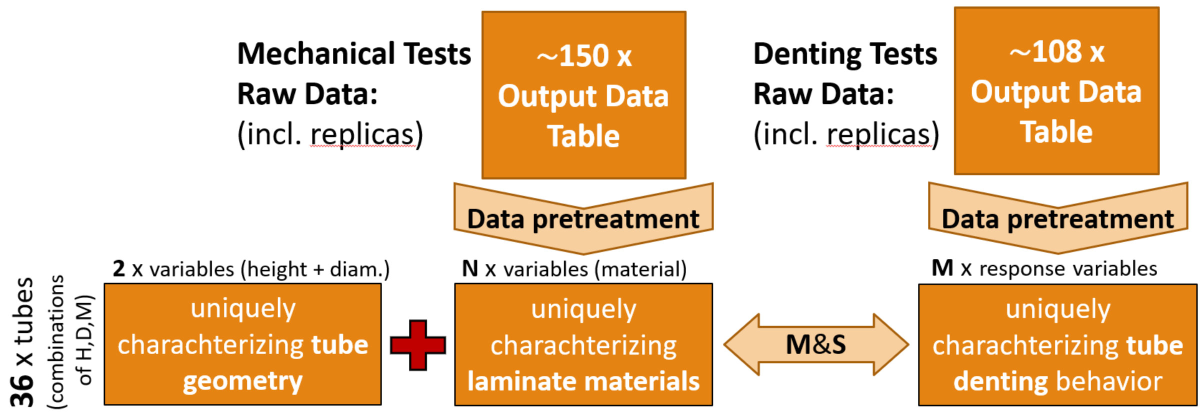


Figure 3.21. *Scheme of the predictive model structure.*

3.5.1 Predictors

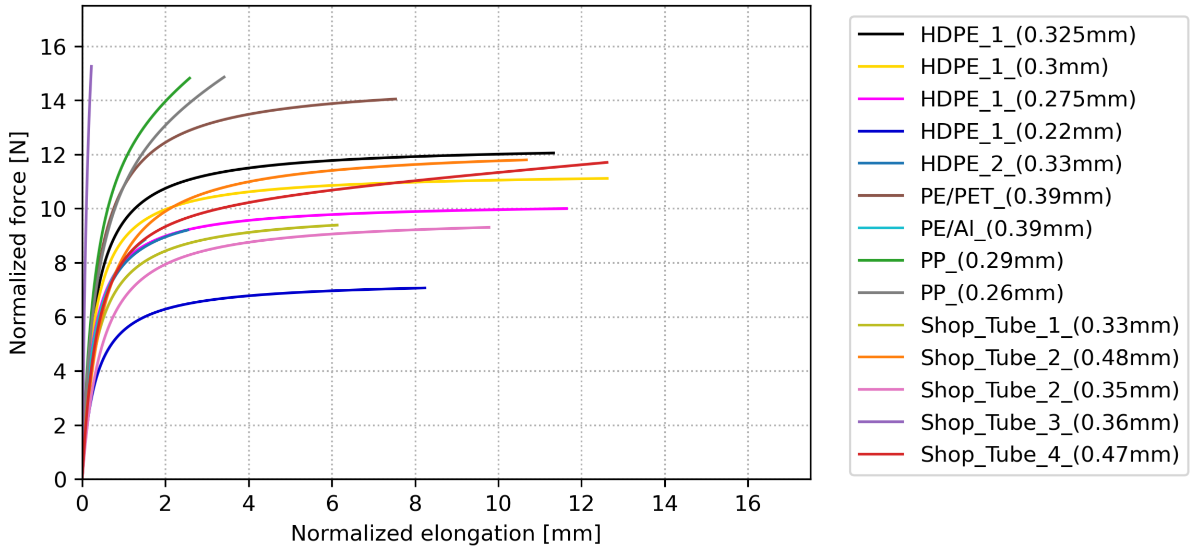
Among the predictors, only the mechanical properties had to be measured, considering that thickness of the material, height, and diameter of the tube are readily available information.
All the relevant information regarding possible data management strategies and data quality is presented in Section 3.3.1. In figure 3.22(a) and 3.22(b) respectively the tensile and bending tests results are presented.

3.5.1.1 PCA: characterization of the materials

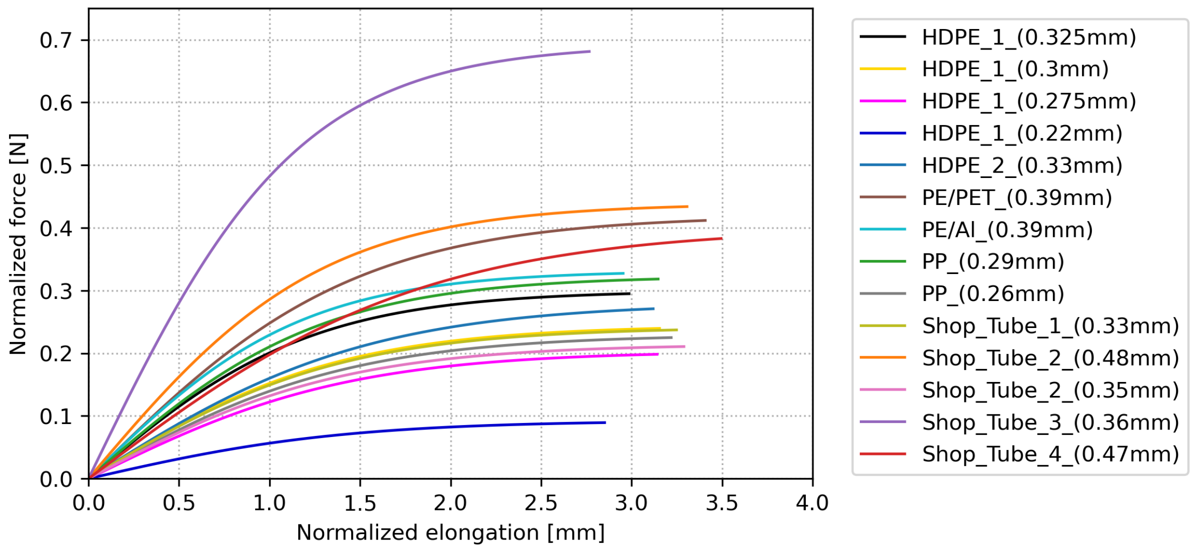
Performing a PCA on the predictors (dataset structure displayed in Table 3.2), we can better characterize the chosen materials, highlighting their differences and proving that the whole group is a representative sample within the class of composite materials they belong to (they cover sufficiently well the principal component space). This is important in a number of ways:

- a better understanding of the studied materials is useful during the development of the predictive model; when performing a PLS it can for instance provide clues for the interpretation of the latent variables.

- a study of the T^2 statistic allows to identify items which are very different from the rest of the calibration dataset, and thus have the potential to influence significantly the predictive model. These items should not be excluded a priori from the dataset, since it's not



(a) *Tensile tests results (fitted curves), performed on all 14 available materials.*

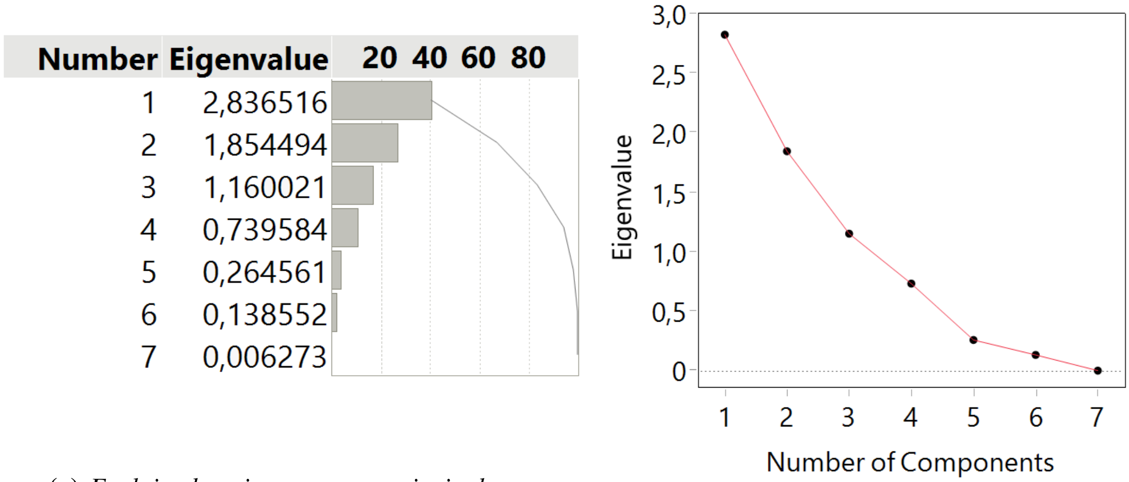


(b) *Bending tests results (fitted curves), performed on all 14 available materials.*

Figure 3.22

necessarily true that they will be outliers also in the predictive model, but their influence will nonetheless have to be thoroughly assessed.

The optimal number of principal components for the model is four; this is suggested both by the explained variance versus principal component plot (Figure 3.23(a)) and by the scree plot (Figure 3.23(b)). The total explained variance with 4 principal components is 94.2%.



(a) *Explained variance versus principal component of the PCA performed on the model predictors.*

(b) *Scree plot of the PCA performed on the model predictors.*

Figure 3.23. *Metrics for the choice of the number of principal components in the PCA performed on the model predictors.*

The score and loading plots are presented in Figure 3.24.

The meaning of the regression parameters (discussed in detail in Section 3.3.1.2) can be summarized as follows:

- **P1**: tensile curve plateau (if no asymptotic component is introduced);
- **P2**: inversely related to the initial slope of the tensile curve;
- **P3**: inversely related to the steepness of the elastic-plastic transition in tensile curves (the curve section influenced by the parameter will be referred to as *elbow*);
- **P4**: related to the slope of the asymptote of the tensile curve;
- **P5**: bending curve plateau;
- **P6**: related to the steepness of the bending curve.

Thanks to a careful observation of such plots it is possible to identify the precise features of the materials which underlie each principal component:

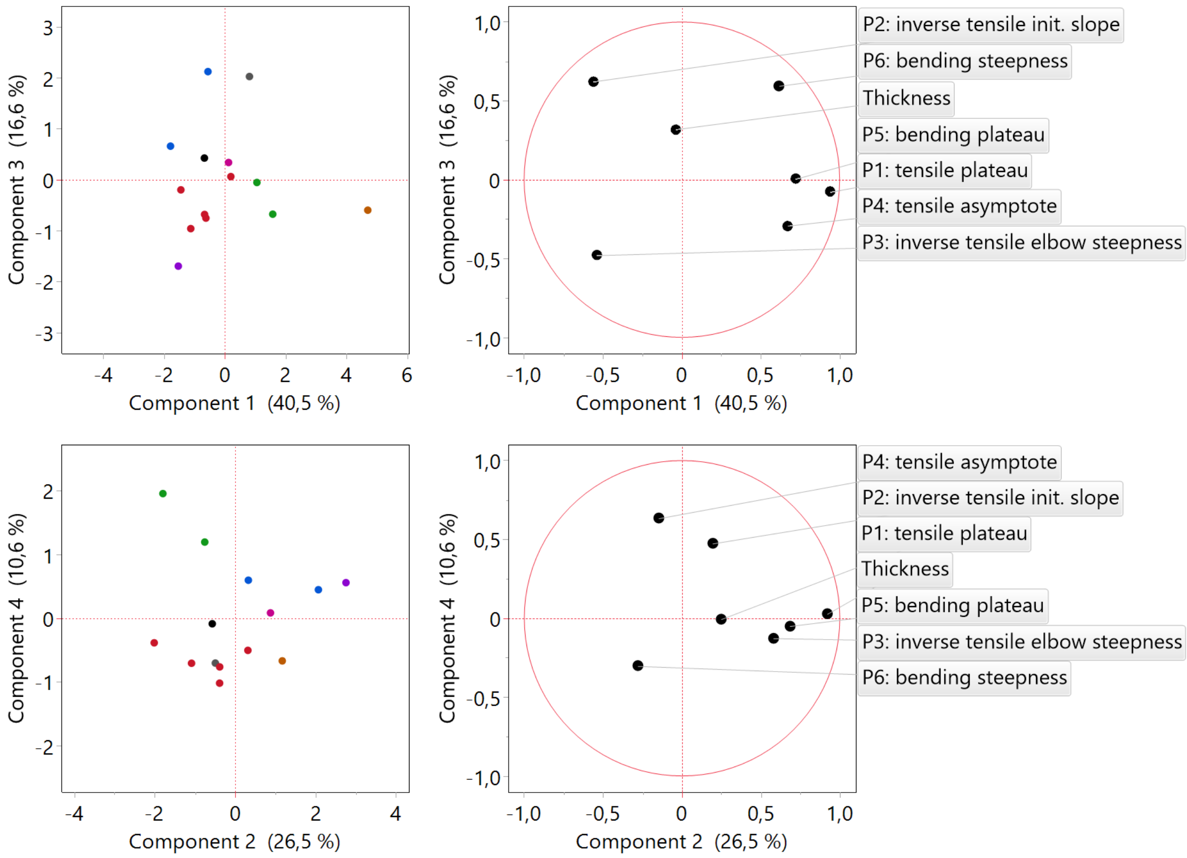


Figure 3.24. *Score and loading plots of the PCA performed on the model predictors; the colors are used to distinguish materials in classes:* ***red****=HDPE/EVOH,* ***magenta****=HDPE/PET,* ***grey****=ABL,* ***green****=PP,* ***black****=Shop Tube 1,* ***blue****=Shop Tube 2,* ***orange****=Shop Tube 3,* ***purple****=Shop Tube 4.*

- **Principal component 1** increases along with coefficients P1, P4, P5, and P6 and decreases with coefficients P2 and P3; it is important to note that these two last coefficients are inversely related to features of the tensile curves, thus their influence is, in reality, coherent with the other four coefficients; the principal component is instead not related to the thickness of the material.

  It can be concluded that the first principal component mainly captures a general trend in the overall intrinsic stiffness of the materials (both in terms of tensile and bending tests and including both the elastic and the plastic deformation domain). Intrinsic refers to the fact that such trend regards the materials independently from their thickness, but only in relation to their mechanical nature.

  This interpretation aligns perfectly with the information provided by the score plot, for instance, Shop Tube 3 (in orange in Figure 3.24(a)) has an extremely high value of principal component 1 and coherently is an outlier in terms of intrinsic stiffness (can be observed in the curve trends in Figure 3.22); the opposite can be said of Shop Tube 4 (in purple).

- **Principal component 2** increases along with material thickness, parameters P3 (inversely related to the steepness of the elastic to plastic transition in tensile curves) and P5 (related to the bending plateau); among all predictors, it is for sure the material thickness which determines its value. In fact, in terms of the second principal component, the scores are almost perfectly aligned with the value of thickness of the corresponding material;

- **Principal component 3** grows for greater values of P2 (inversely related to tensile stiffness) and P6 (steepness of the transition from elastic to plastic behavior in bending curves), while decreases with P3; it is instead not affected at all by the values of the plateaus (P1 and P5).

  It appears that the third principal component is mainly related to the steepness of the transition from elastic to plastic behavior, both regarding tensile and bending tests; clearly, the transition is even steeper having a fixed value of the plateau and a lower value of initial stiffness (this explains the loading on predictor P2).

  It can be concluded that the principal component is related to the extent to which the material is capable of elastic (linear) deformation up to a certain yield point, over which a steep transition to plastic behavior takes place.

  This property is evaluated independently from the material thickness and the maximum force that the material can withstand (plateau values).

  Materials such as Shop Tube 4 readily deform plastically, and thus present a low value of the third principal component score; instead, materials containing stiff barrier layers, such as ABL, present a larger elastic range and consequently a higher score. In this regard, the characterization that the model provides regarding Shop Tube 3 is incorrect; this is because such material doesn't present at all a plastic behavior in tensile tests (it is rigid and brittle), nonetheless the fitting functions are formulated for plastic materials and consequently return a coefficient describing the steepness of the elastic-plastic transition; such parameter ends up being not representative of reality. Then, the third principal component interprets the value of the parameter as an indication that Shop Tube 3 presents a smooth elastic-plastic transition, while it is well-known and proven that materials containing cellulosic components are rigid. This issue might very well compromise the predictions performed on Shop Tube 3 and on similarly rigid materials.

- **Principal component 4** increases with coefficients P2 (inversely related to tensile stiffness) and P4 (related to the slope of the asymptote of the tensile curves).

  This leads to the conclusion that the fourth principal component mainly distinguishes materials in terms of their asymptotic behavior in tensile tests. These trends are in practice related to the phenomena of strain hardening and necking, which takes place to different extents in different polymeric materials (clustering according to the classes of materials is in fact quite evident in Figure 3.24(c)).

This interpretation is confirmed by the fact that PP, and Shop Tube #2 and #4 display a high value of the fourth principal component and at the same time are the only materials presenting an asymptotic trend in tensile tests.

To confirm the capability of the model of capturing in a quite general way the mechanical properties of the tested materials, the Q statistic is studied (Figure 3.25). All samples display a moderate distance from the model space, consequently the model can be regarded as adequate.

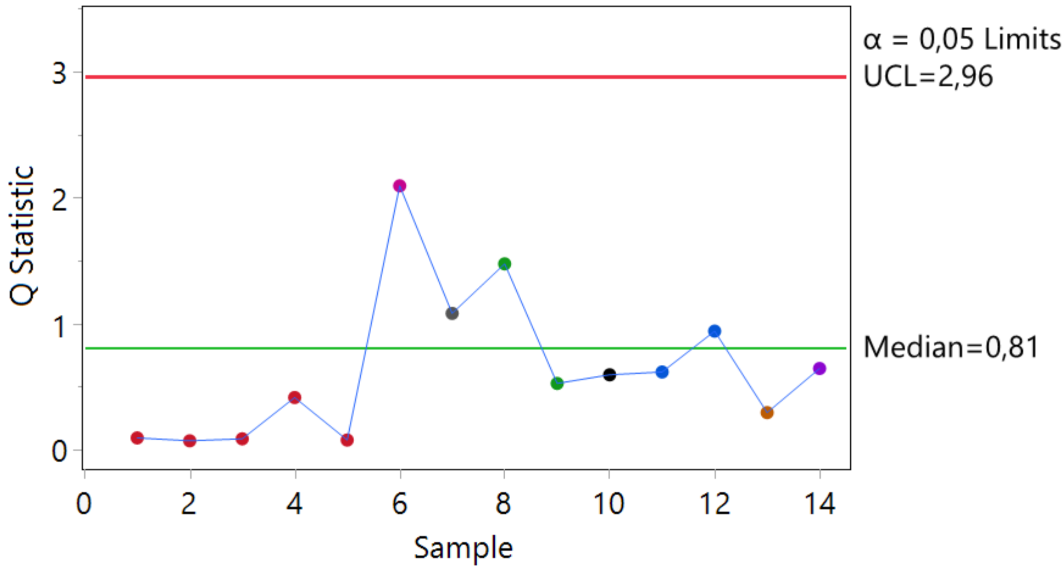


Figure 3.25. *Q statistics of the PCA performed on the model predictors; the colors are used to distinguish materials in classes:* ***red****=HDPE/EVOH,* ***magenta****=HDPE/PET,* ***grey****=ABL,* ***green****=PP,* ***black****=Shop Tube 1,* ***blue****=Shop Tube 2,* ***orange****=Shop Tube 3,* ***purple****=Shop Tube 4.*

Having confirmed the meaningfulness of the PCA results, it is reasonable to use the model to assess the presence of outliers within the predictors data. For this task the T^2 statistic is studied (Figure 3.26).

Predictions performed on samples which, under some important aspects, differ heavily from the rest of the group (outliers) might lead to poor results. This is not always the case, and very much depends on whether these aspects are relevant for the response, nonetheless, it is reasonable to put particular care into the evaluation of the results derived from predictions on samples which are outliers in the predictors dataset.

In this specific instance, this is the case for Shop Tube 3 and Shop Tube 4. Similar observations should be performed on newly tested materials before performing predictions regarding their denting performance.

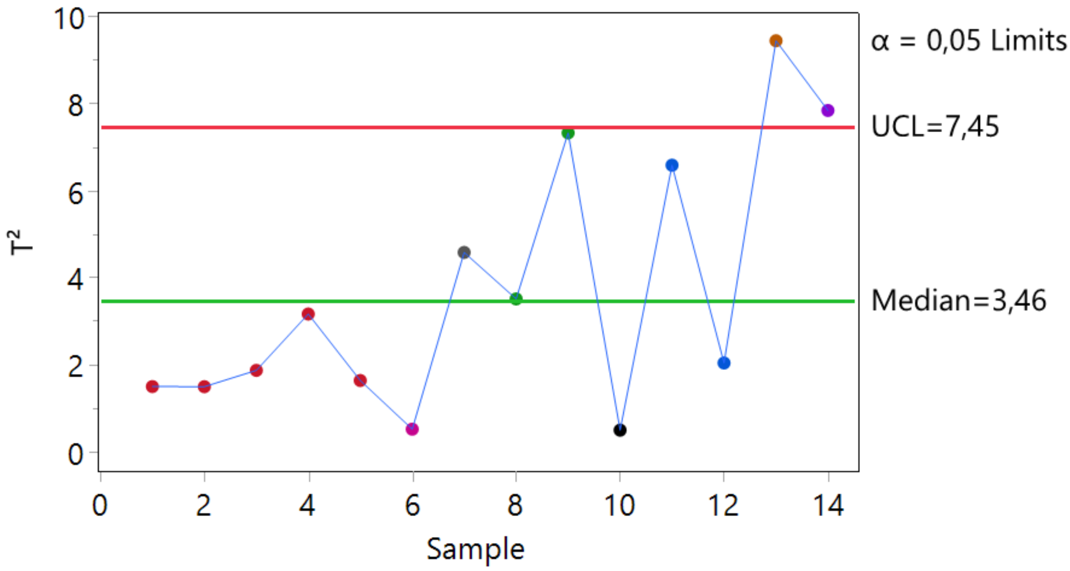


Figure 3.26. *T^2 statistics of the PCA performed on the model predictors; the colors are used to distinguish materials in classes:* ***red****=HDPE/EVOH,* ***magenta****=HDPE/PET,* ***grey****=ABL,* ***green****=PP,* ***black****=Shop Tube 1,* ***blue****=Shop Tube 2,* ***orange****=Shop Tube 3,* ***purple****=Shop Tube 4.*

The T^2 contribution proportions of the outliers are also examined (Figure 3.27). These plots are helpful in identifying the deviating features of each outlier, the results correspond with what was expected:

- PP - 290μm presents a peculiar strain hardening behavior;
- Shop Tube 2 - 480μm is particularly thick and nonetheless surprisingly compliant (in tensile terms);
- Shop Tube 3 - 360μm presents an incredibly high stiffness (expected from cellulosic composite materials), as well as no plastic compliance, meaning that the plateau parameters are abnormally high;
- Shop Tube 4 - 470μm presents a very soft transition from elastic to plastic behavior, thus low values of parameters P3 and P6; this is expected considering the elastomeric nature of some layers of the material.

3.5.2 Responses

The denting test data, measured on an adequate set of tubes, constitutes the response dataset of the model; namely, for each combination of the key variables, such data quantifies the denting performance of the corresponding tube.

Regarding the choice of factors to be studied, the same considerations regarding variables a priori selection discussed for the screening test (Section 3.4.1) apply here.

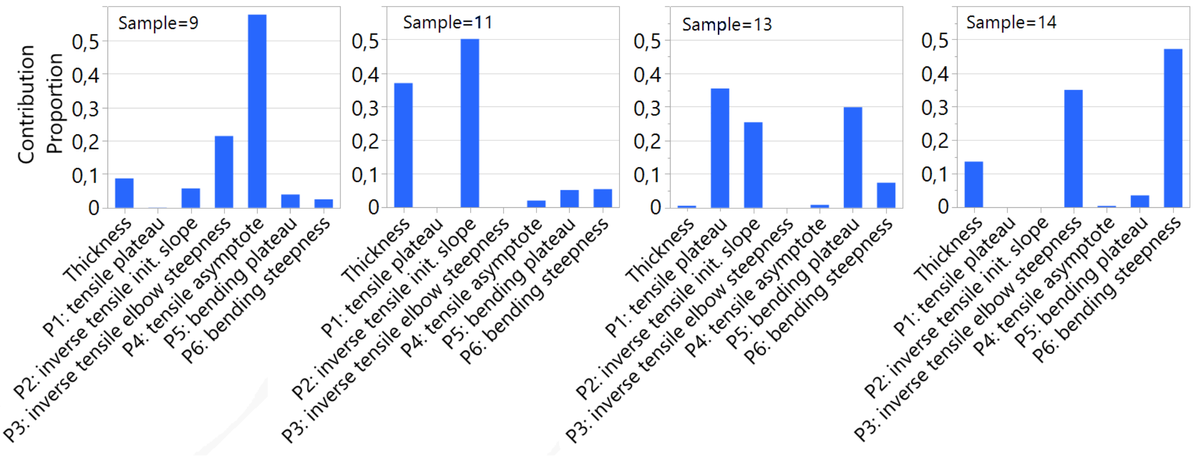


Figure 3.27. *T^2 statistics contribution proportions for materials PP - 290*µm *(sample 9), Shop Tube 2 - 480*µm *(sample 11), Shop Tube 3 - 360*µm *(sample 13), Shop Tube 4 - 470*µm *(sample 14)*

Moreover, thanks to the conclusions drawn from the screening test itself, the reasoning can be brought a step further, also excluding the factor *bulk* (it is acceptable to choose one conditioner for all tubes) and performing replicas on already tested tubes.

The remaining three factors are allowed to vary on as many levels as it was practically possible:

- **material (mechanical properties)**: 14 levels corresponding to the 14 materials available;
- **tube diameter**: 2 levels (40mm and 50mm), corresponding to the formats commonly used for conditioners (D40 and D50);
- **tube body height** 3 levels (14.5cm, 16.5cm, 18.5cm) for D50 tubes and 2 levels for D40 tubes (14.5cm, 16.5cm), corresponding to the range of values commonly available; in some cases, the actual values slightly differ from the levels described above (for reasons related to sample preparation); this is not an issue considering that the variable is continuous.

Ideally, the factors should be varied along all combinations of the levels (full factorial design); unfortunately, not all materials are available as tubes in all diameters and heights; if the height is greater than what's needed, the tube can be cut, but if it is too short, nothing can be done. This meant that only a fraction of all 70 combinations of the factors were available to test (36 in total).

For each combinations, three replicas were performed (on the same tube).
The final experimental design is presented in Table 3.11.
All the relevant information regarding possible data management strategies and data quality is presented in Section 3.3.1.

Table 3.11. *Randomized experimental design for response data collection (denting performance predictive modelling); the test on each sample was replicated two times for a total of 108 tests.*

Sample	Body height [cm]	Diameter [mm]	Material
1	18.5	50	ABL - 390µm
2	14.5	40	HDPE Lam. 1 - 275µm
3	14.5	50	HDPE Lam. 2 - 330µm
4	16.5	40	HDPE Lam. 1 - 275µm
5	14	40	HDPE Lam. 1 - 220µm
6	14	50	Shop Tube 2 - 480µm
7	14.5	50	Shop Tube 1 - 330µm
8	16.5	50	PP - 290µm
9	14.5	40	HDPE Lam. 1 - 325µm
10	18.5	50	HDPE Lam. 1 - 300µm
11	14	50	Shop Tube 2 - 350µm
12	18.5	50	PP - 260µm
13	14.5	50	HDPE Lam. 1 - 325µm
14	16.5	50	PP - 260µm
15	14.5	50	ABL - 390µm
16	14.5	50	PP - 290µm
17	16.5	50	PE/PET - 390µm
18	14.5	50	PP - 260µm
19	18.5	50	PE/PET - 390µm
20	18.5	50	HDPE Lam. 1 - 325µm
21	16.5	40	HDPE Lam. 1 - 325µm
22	15.5	40	Shop Tube 4 - 470µm
23	16.5	40	HDPE Lam. 1 - 300µm
24	18.5	50	PP - 290µm
25	16.5	40	ABL - 390µm
26	16.5	50	Shop Tube 1 - 330µm
27	14.5	40	ABL - 390µm
28	16.5	50	ABL - 390µm
29	14.5	50	PE/PET - 390µm
30	16.5	50	HDPE Lam. 1 - 300µm
31	14.5	50	HDPE Lam. 1 - 300µm
32	14.5	50	Shop Tube 3 - 360µm
33	16.5	40	HDPE Lam. 1 - 220µm
34	14.5	40	HDPE Lam. 1 - 300µm
35	16.2	50	HDPE Lam. 1 - 325µm
36	16.2	50	HDPE Lam. 2 - 330µm

In Figure 3.28 the obtained fitted denting curves are presented, they are split into four plots just to make it possible to follow individual curves.

To provide an easier visualization of the effects of tube body height, diameter, and material, color-mapped versions of the denting curves data are presented in Figure 3.29.

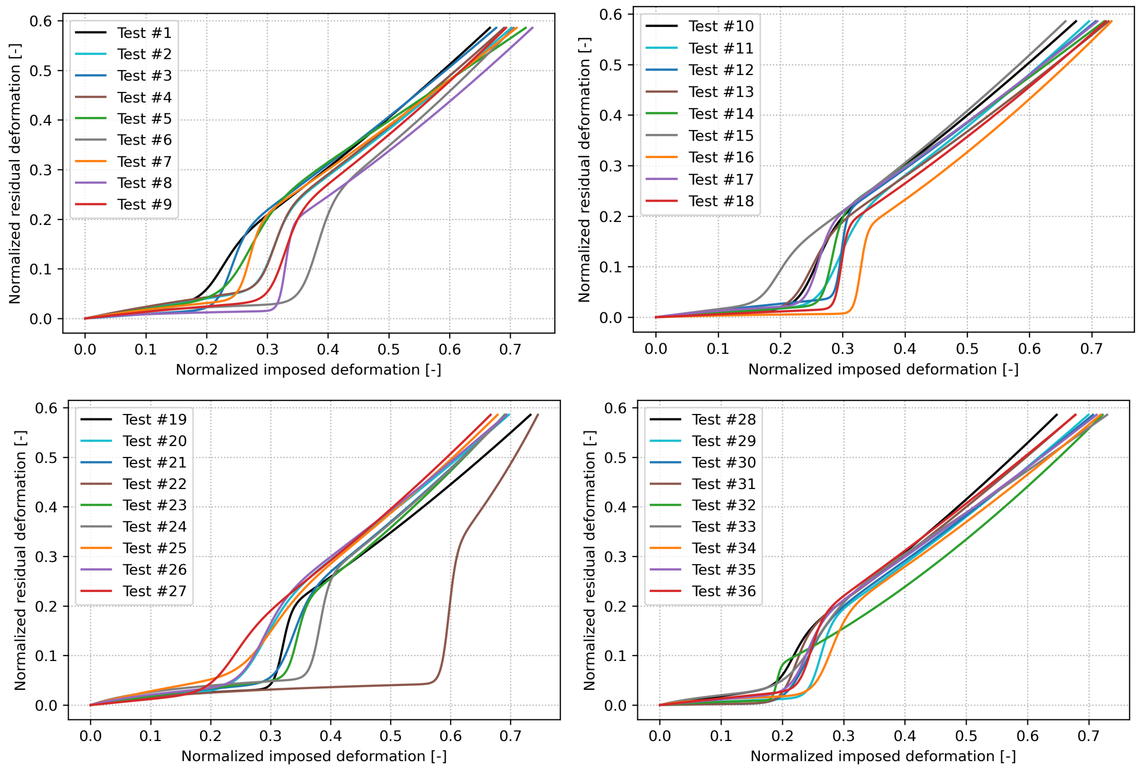


Figure 3.28. *Fitted denting curves corresponding to the experimental design presented in Table 3.11. The curves are displayed in four plots just to make it easier to distinguish among them.*

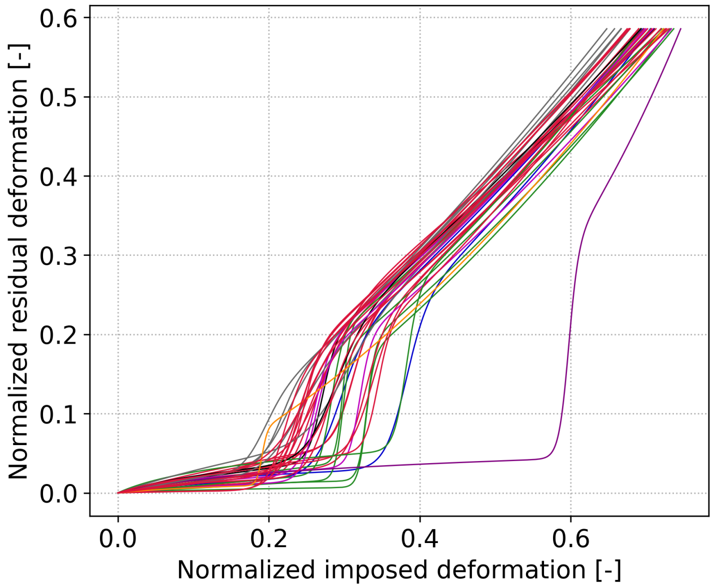
3.5.3 Data management for predictive modelling

Data management has already been presented both for mechanical and denting data, but, to develop a predictive model, the two datasets have to be joined, and a different format of either the predictors or the responses can have profound consequences on the quality of the results. This is mainly due to limitations in the capability of the modelling technique to extract information from one or the other arrangement of the data; in the case of PLS, the main limitation is related to a high degree of non-linearity in the data, which the methodology can not efficiently deal with given its linear nature.

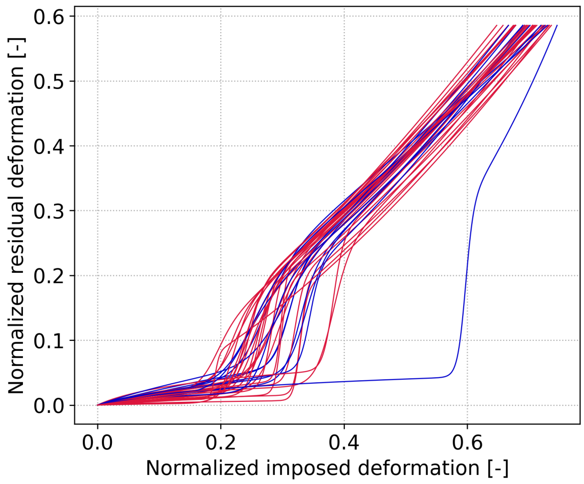
3.5.3.1 Summary of predictors and responses formats and possible combinations

Let's summarize the available formats:

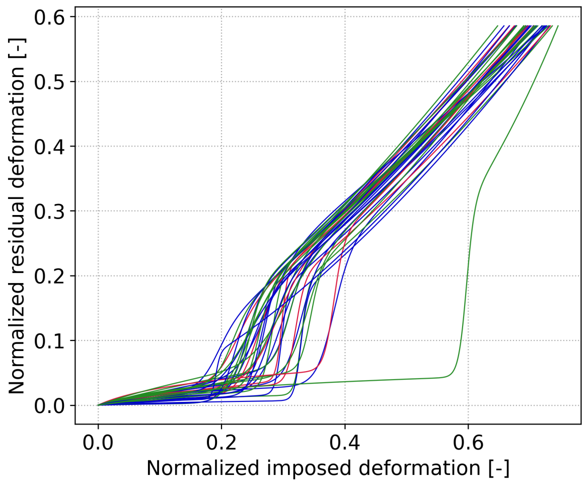
- for the predictors, the only strategy which allows to retain all data is to use directly the regression coefficients of the mechanical force/elongation tests (Section3.3.1.2);



(a) *Colors distinguish the denting curves by material classes:* ***red****=HDPE/EVOH,* ***magenta****=HDPE/PET,* ***grey****=ABL,* ***green****=PP,* ***black****=Shop Tube 1,* ***blue****=Shop Tube 2,* ***orange****=Shop Tube 3,* ***purple****=Shop Tube 4.*



(b) *Colors distinguish the denting curves by diameter:* ***blue****=40mm,* ***red****=50mm.*



(c) *Colors distinguish the denting curves by height:* ***red****=14.5cm,* ***green****=16.5cm,* ***blue****=18.5cm.*

Figure 3.29. *Fitted denting curves with color mapping to visualize the effect of the key variables under study.*

- the response data (denting curves) can be used both in the form of aligned data (along x or y axis) or in form of regression coefficients (Section 3.3.2.2).

It follows that a series of datasets for predictive modelling can be obtained by joining the predictors with the different formats of the responses:

1. three different datasets are obtained by combining the predictors with one out of the three responses formats;

2. other four datasets are possible by joining the predictors dataset with a new response dataset obtained concatenating couples or even all three responses formats.

The choice of the best option is ultimately determined by the performance of the associated model, nonetheless, some observations on the characteristics of each format can help in understanding the reasons behind the superiority of one strategy over the others.

3.5.4 Partial Least Square model

The modelling methodology of choice is PLS, this can not only provide a model for the prediction of denting performance, but also helps in understanding the influence of the mechanical properties of the constituent material.

3.5.4.1 Choice of the dataset format

Out of the first group of possible formats, the dataset obtained using the y-aligned responses (along the residual deformation axis) is the best performing one; in fact, by identifying 6 latent variables, it manages to explain 75% of the responses variability with 88% of the predictors variability (see Figure 3.30(c)).

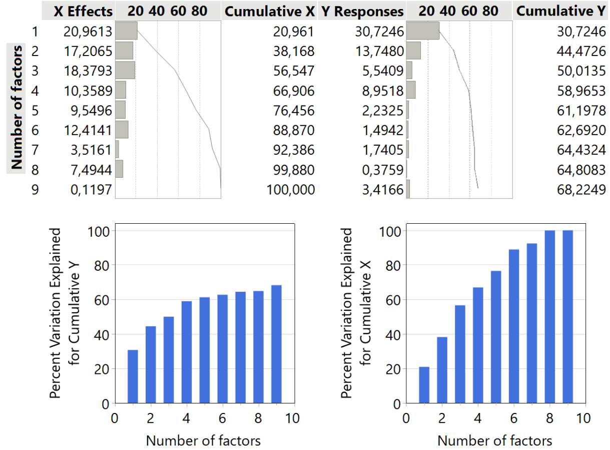
Even though the approaches belonging to the first group are definitely simpler and still capable of providing good results, there are multiple reasons for adopting the ones of the second group (particularly the one including all three data formats):

- the response format containing the denting curves regression coefficients proves to be the least adequate to be used stand alone as response dataset in PLS modelling (see Figure 3.30(a));

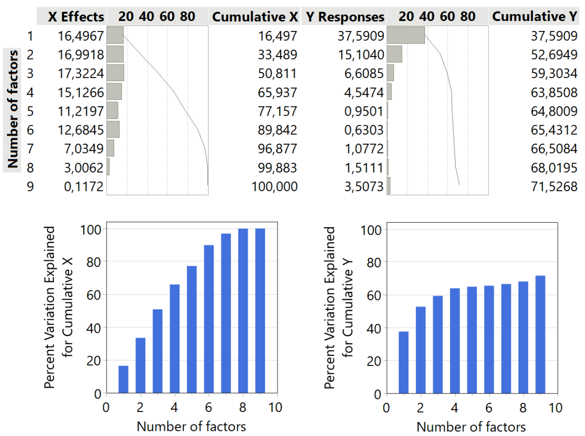
- choosing either one or the other alignment format leads to assigning different weights to different sections of the denting curves; this is due to the fact that each section of the denting curves ends up being associated with a number of response variables related to the slope of such section. This is easily observed in Figure 3.11, where, relatively to a x-wise alignment, many more variables are associated with the flat parts of the curve (beginning and end) than with the indentation point (middle).

  By using simultaneously both the x-aligned and the y-aligned response formats (each one including the same number of variables) this issue is solved. The parts of the curve least characterized by one format are well-described by the other.

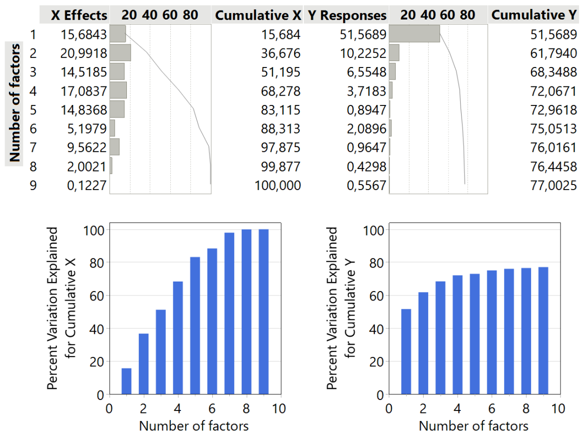
  Other solutions to this issue exist, such as an accurate choice of the alignment vector, which can be tuned in order to correspond to more or less equispaced points of the denting



(a) *Responses format containing the regression parameters of the denting curves.*



(b) *Responses format containing the x-aligned values of the denting curves (residual deformations aligned along fixed imposed deformation values).*



(c) *Responses format containing the y-aligned values of the denting curves (imposed deformations aligned along fixed residual deformation values).*

Figure 3.30. *Predictors and responses cumulative explained variability for PLS models developed using different responses formats.*

curves, nonetheless, these strategies are not as general (such vector may not perform as well against significantly different denting curves) nor as simple.

- the redundancy of information due to the simultaneous use of three different formats of the same response dataset it's not a problem for machine learning techniques such as PLS, which can handle a high degree of collinearity; actually, such redundancy is beneficial because, if some piece of information cannot be captured by the methodology in one format, it is available in the others under a different form (potentially easier to capture). This renders the model more robust than any of the other alternatives.

A six latent variables model developed through this strategy can explain 71.34% of the responses variability by using 92% of the variability of the predictors; this is slightly less than what is obtained using as response dataset just the y-aligned vector of imposed deformations (Figure 3.31). A slight decrease in response explained variability was nonetheless expected given that all three responses formats contribute to the addition of unexplained variability. Ultimately, the model's capability of correlating predictors and responses can be regarded as satisfactory.

Regarding the considerable fraction of unexplained response variability, it is most likely related to non-linearities in the data correlation structure; this could be confirmed in future studies on the dataset, using non-linear modelling techniques. The unexplained variability associated to experimental errors in the denting and mechanical measurements is very likely limited, given the proven accuracy of the tests. Similarly, it appears unlikely that impactful factors were overlooked.

Number of factors	X Effects	20 40 60 80	Cumulative X	Y Responses	20 40 60 80	Cumulative Y
1	16,4015		16,402	48,0540		48,0540
2	18,5579		34,959	11,9973		60,0513
3	15,6529		50,612	6,4183		66,4696
4	15,0925		65,705	3,3584		69,8280
5	15,4485		81,153	0,8056		70,6336
6	10,8486		92,002	0,7143		71,3479
7	2,5254		94,527	1,7315		73,0794
8	5,3568		99,884	0,5506		73,6300
9	0,1158		100,000	2,8226		76,4526

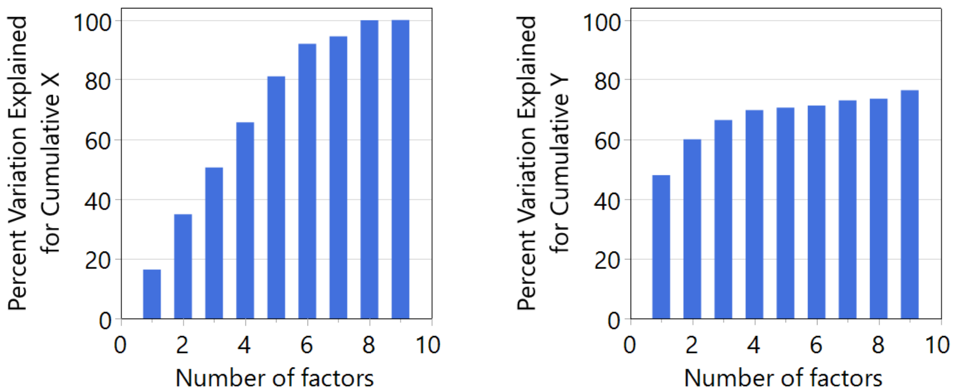


Figure 3.31. *Predictors and responses cumulative explained variability for the PLS model developed using simultaneously as response dataset all different formats of the response data (denting curves regression parameters, x-aligned residual deformations, and y-aligned imposed deformations).*

All of the above is supported by a better explanatory and predictive performance of the model (when adopting as response dataset the combination of all three formats), as displayed in Figure 3.32). This further motivates the choice of this version of the response dataset for the development of the final model.

3.5.4.2 Number of latent variables

Having confirmed the choice of the dataset for model development, it follows that an adequate number of latent variables is to be chosen and interpreted.

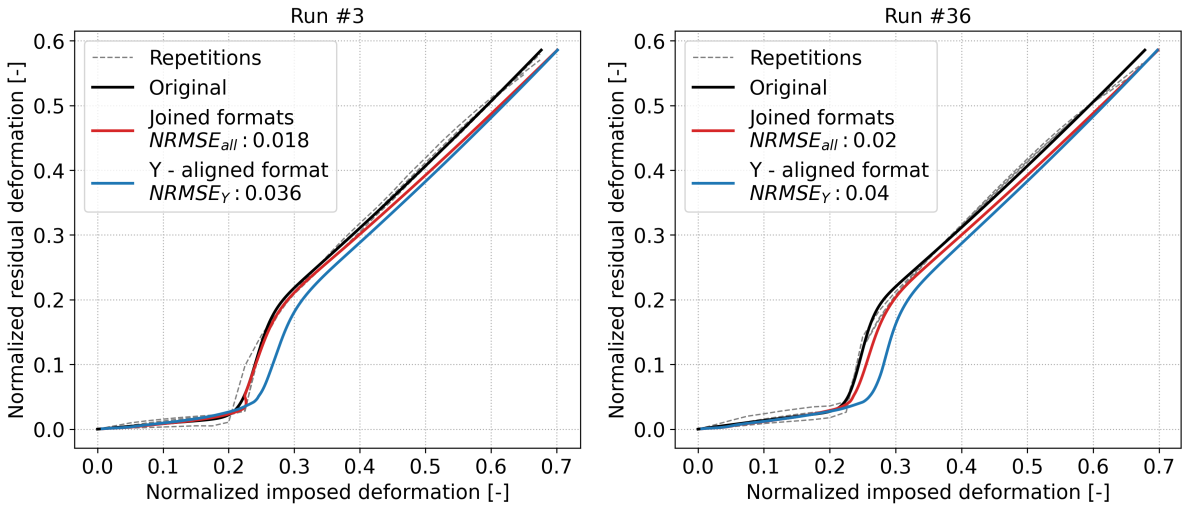


Figure 3.32. *Preview of the predictive capabilities of the PLS model, highlighting the enhanced predictive performance obtainable employing the response dataset composed joining all three possible formats of the responses. To identify the features of the tubes corresponding to each run refer to Table 3.11.*

Other than the explained variability versus number of factors plot (Figure 3.31), also the results of NIPALS Cross Validations can be used to evaluate the relevance of each latent variable and thus choose their amount (Table 3.12). The algorithm suggests to use just four principal components, this is related to the limited amount of explained response variability of the subsequent latent variables; nevertheless, six latent variables are chosen, this is due to a couple of reasons:

- latent variables 5 and 6 are related to a significant amount of the predictors variability, thus they are definitely relevant for model inversion purposes;
- the amount of explained variability in the responses is to be taken as an indication of the potential relevance of a latent variable, but it doesn't necessarily represent it truthfully. Namely, if an important but very confined section of the denting curve is represented by latent variables 5 and 6, it is expected that the associated explained variability is small, given that only a handful of variables will be associated with such section; this doesn't mean that the two latent variables are worthless;

This led to the conservative choice of keeping 6 latent variables, also considering that for all of them an interpretation can be provided.

3.5.4.3 Score plots, loading plots and latent variables interpretation

Score plots (Figure 3.33) and loading plots (Figure 3.34, 3.35, and 3.36) are instrumental in understanding the correlation structure identified by the modelling methodology.

Figures 3.37 and 3.38 are also extremely helpful: they display in a very intuitive way the fraction of the variability of each variable that is explained by the individual latent variables. This is directly related to the loadings, and thus proves very helpful in the interpretation of the latent variables. Figure 3.38 in particular has proved of great usefulness, since it allows

Table 3.12. *Results of cross-validation of the PLS model through the NIPALS algorithm.*

Number of factors	Root Mean PRESS	van der Voet T^2	Prob > van der Voet T^2	Q^2	Cumulative Q^2	R^2X	Cumulative R^2X	R^2Y	Cumulative R^2Y
0	1,028571	11,629694	0,0050*	-0,057959	-0,057959	0,000000	0,000000	0,000000	0,000000
1	0,946714	10,646079	0,0050*	0,188743	0,188743	0,166421	0,166421	0,480936	0,480936
2	0,898277	11,080139	0,0010*	0,272577	0,409873	0,187321	0,353743	0,119023	0,599959
3	0,846552	13,215215	0,0010*	0,239129	0,550990	0,157169	0,510911	0,065410	0,665370
4	0,815927	0,000000	1,0000	0,379937	0,721585	0,149497	0,660408	0,034806	0,700176
5	0,841920	7,236552	0,0550	0,311820	0,808400	0,151096	0,811505	0,009098	0,709273
6	0,868208	4,581652	0,3100	0,125101	0,832370	0,107103	0,918608	0,007720	0,716993
7	0,894741	4,210198	0,3710	0,141279	0,856052	0,032753	0,951361	0,015653	0,732646
8	0,889223	2,034386	0,8120	0,357157	0,907464	0,047483	0,998844	0,007007	0,739653
9	0,903503	4,792913	0,3010	0,332056	0,938191	0,001155	1,000000	0,028109	0,767760

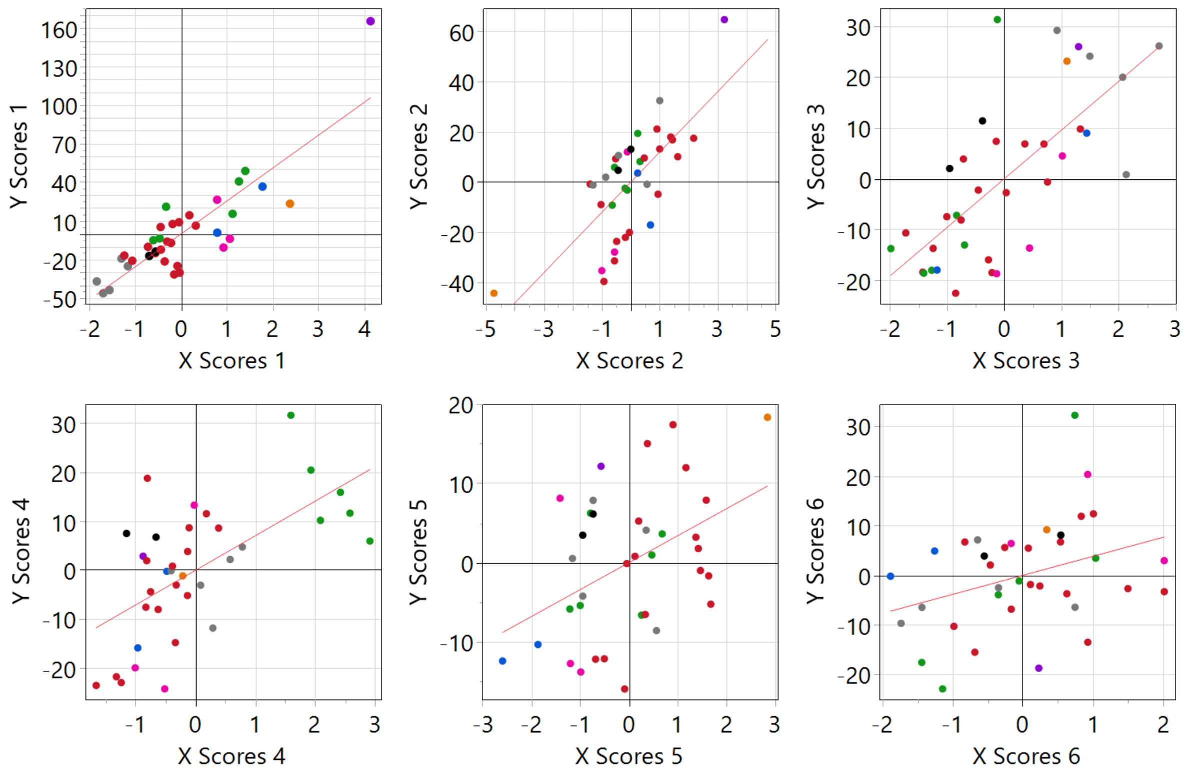
to evaluate whether the latent variable under study "shifts" a particular section of the curve upwards/downward (in the case in which the explained variability is more significant on the x-aligned plot than on the y-aligned plot) or to the left/to the right (in the opposite case).

- **Latent variable 1:** by studying the loadings it appears that the first latent variable is responsible for the position of the indentation point in terms of imposed deformation. Namely, higher values tend to shift the indentation point and consequently the remaining part of the curve "to the right" (in terms of imposed deformation); this is confirmed by the fact that the value of the loadings are more or less stable from the indentation point on, meaning that the latent variable doesn't have a marked impact on a specific point, but affects the section as a whole. The interpretation is confirmed by the scores values, for instance, the unusually high score of Shop Tube 4 (purple) corresponds to a denting curve highly shifted "to the right", conversely, the negative scores of ABL (gray) reflect denting curves shifted "to the left". It is noteworthy that the model is not fully capable of capturing the behavior of Shop Tube 3 (orange), which in fact presents a denting markedly shifted to the left and is instead assigned a high score; given the markedly different nature of the material with respect to the sample average, this is reasonable.

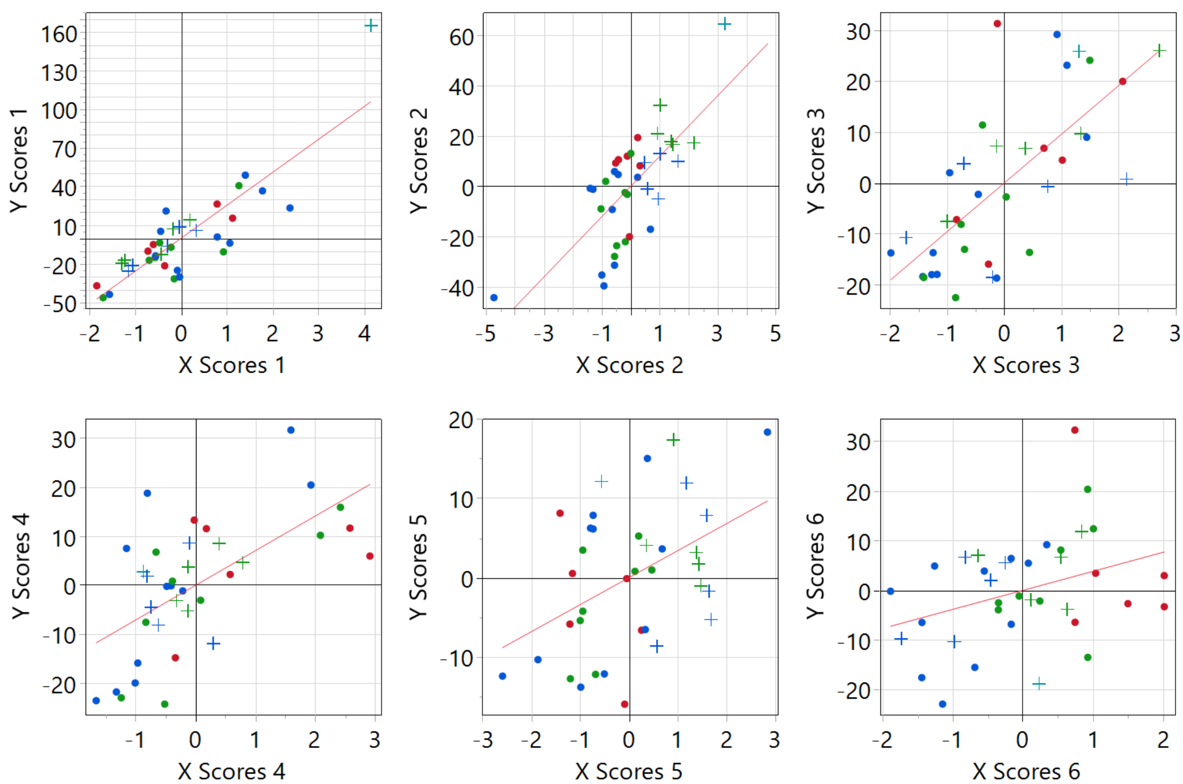
  Let's now study the predictors score plot to assess which factors mostly affect the first latent variable: while it is not influenced by the geometry of the tube, it is influenced by the mechanical properties of the materials; specifically, it increases for:

  - less steep transitions from elastic to plastic behavior in tensile tests (P3), which can be associated with a lower "proportional limit" strength of the material;
  - lower values of the bending stiffness;
  - higher values of yield strength, both in tensile and bending tests (P1 and P5);
  - a greater thickness of the material.

  The key learning is that the insurgence of the indentation is discouraged in materials which slowly transition to a plastic behavior and possess a high yield strength; these



(a) *Colors distinguish the scores by material classes:* ***red****=HDPE/EVOH,* ***magenta****=HDPE/PET,* ***grey****=ABL,* ***green****=PP,* ***black****=Shop Tube 1,* ***blue****=Shop Tube 2,* ***orange****=Shop Tube 3,* ***purple****=Shop Tube 4.*



(b) *Markers distinguish the scores by diameter, colors by body height:* ***cross****=40mm,* ***dot****=50mm;* ***blue****=14.5cm,* ***green****=16.5cm,* ***red****=18.5mm.*

Figure 3.33. *Predictors versus responses score plots of the PLS model (repeated for different color mapping).*

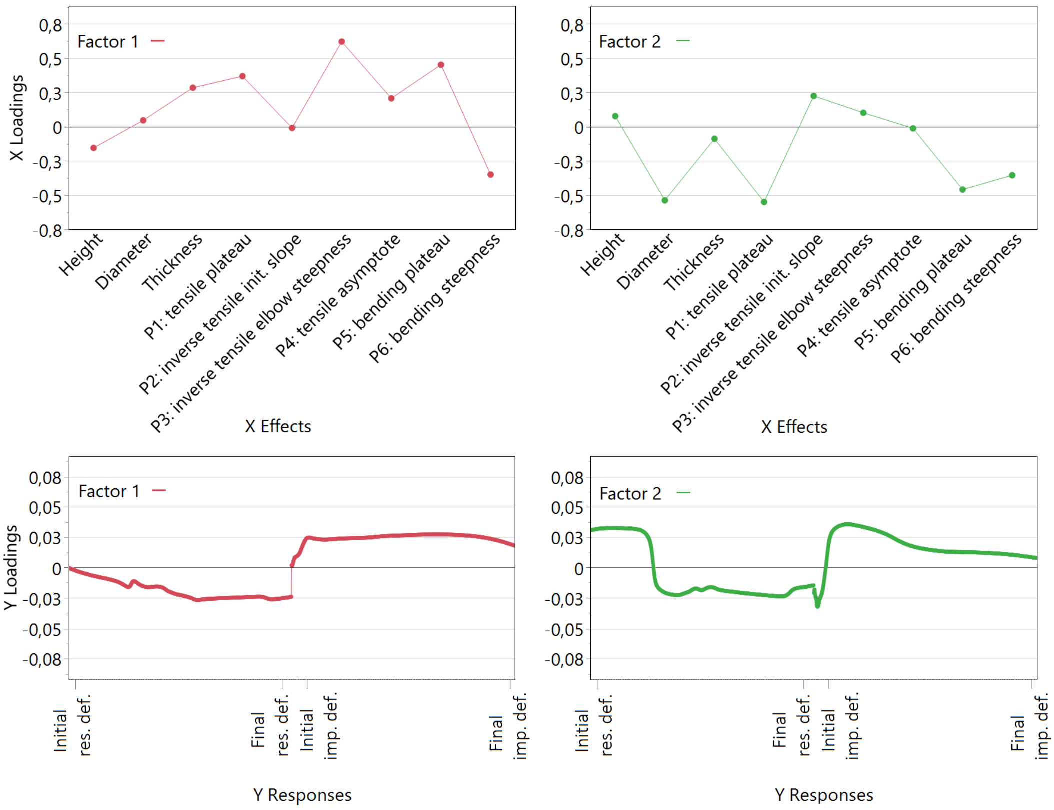


Figure 3.34. *Predictors and responses loading plots for the latent variables 1 and 2 of the PLS model.*

dependencies are coherent with the expectations, given that they tend to prevent the concentration of the stresses in "weak points", which would yield (leading to the indentation), and instead help the tube structure in holding and deforming as a whole.

- **Latent variable 2:** by studying the loadings it appears that the second latent variable is related to the initial section of the denting curve, up to just after the indentation has happened. Specifically, higher values of the second latent variable are related to a higher initial slope of the denting curve and a lower steepness of the indentation. Overall this implies that tubes with a higher value of the second principal component tend to present visible deformations even for small imposed deformations; on the other side, they present a less sharp indentation, which prevents the formation of superficial defects upon large imposed deformations. This means that an average value of the latent value is desirable and both extremes are problematic. This interpretation is confirmed for instance by the high scores of ABL (gray) and the low score of Shop Tube 3 (orange), whose denting curves trends are coherent with the behavior described above. Shop Tube 4 (purple) instead presents a very high score, which does not correspond to a likewise "soft" indentation steepness; in this regard, the model fails to characterize the sample. Once again, given that the material is peculiar, this was expected, and more samples with similar characteristics should be introduced in the dataset in order to enhance the capabilities of the model.

The second latent variable grows for:

– lower tube diameters;

– lower values of yield strength, both in tensile and bending tests (P1 and P5);

– lower bending stiffness.

The key learning is that the promptness of the indentation is heavily dependent on tube diameter: greater diameters are related to a greater initial tolerance to small deformations but are also bound to a more sudden indentation. Also material properties play a role, with materials with a higher yield strength and bending stiffness being once again more resilient to small imposed deformations and then suddenly yielding. Both dependencies are completely reasonable.

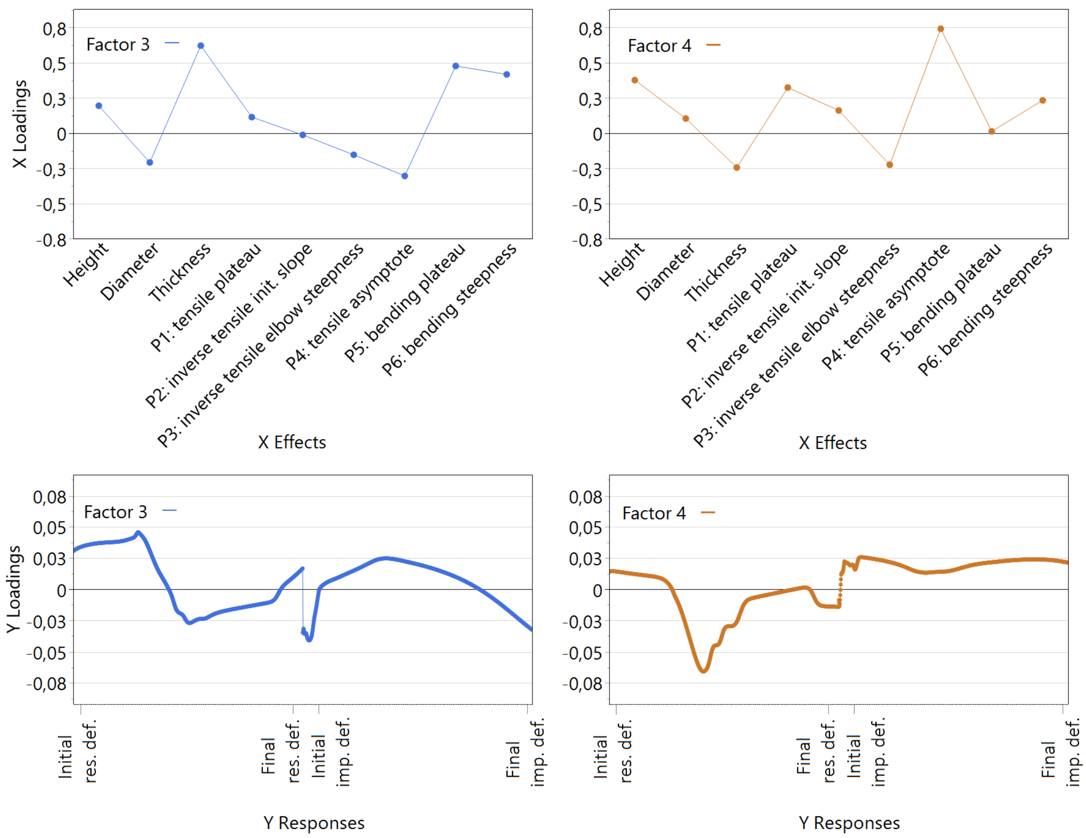


Figure 3.35. *Predictors and responses loading plots for the latent variables 3 and 4 of the PLS model.*

- **Latent variable 3:** by studying the loadings it can be concluded that the third latent variable is mostly responsible for the initial slope of the denting curve; namely higher scores are related to a greater slope in the initial part of the curve (up to the indentation point). This is confirmed by comparing the scores with the trends of the denting curves: PP (green) have for instance low scores and the corresponding denting curves have a small initial slope. The opposite is true for ABL (gray) and Shop Tube 4 (purple). Shop Tube 3 (orange) once again fails to be characterized adequately, displaying a high score instead of a low one (expected); probably this is because of the very "early" indentation that characterizes the tube, which leads to a poor characterization in terms of score. Very likely, in fact, its high score is related to a misinterpretation of some values of the curve, which are after the indentation but are read by the model as if they were before.

The third latent variable grows for:

- greater material thicknesses;
- greater bending stiffness and yield strength.

The key learning is that tubes are more likely to retain small imposed deformations when they are composed of a material which is thick or has a high bending stiffness; apart from extreme cases, this conclusion is not as relevant as the previous ones (for the sake of understanding the phenomenon of denting); in fact, the retention of small imposed deformation is not likely to cause any significant defect on the item.

- **Latent variable 4:** by studying the loadings it can be concluded that the fourth latent variable is related to lower than average values of the section of the denting curve which concerns the indentation point. Specifically, it identifies a correlation between the strain-hardening behavior of PP in tensile tests (related to parameter P4) and greater resilience to denting, which could not be explained otherwise. The scores related to other materials range around zero and do not highlight any other similar behavior.

  The key learning is that tubes are more adverse to denting if they are composed of a material with strain hardening behavior; this can be expected, considering that such property contrasts the local yielding of the material, which is ultimately the cause of the indentation.

- **Latent variable 5:** by studying the loadings it can be concluded that the fifth latent variable is related to the small section of the denting curve where the indentation takes place. Higher scores are related to a sharper indentation taking place earlier and contribute to the characterization of materials such as Shop Tube 3 (orange), whose variability wasn't really explainable by means of the previous latent variables. Nonetheless, the latent variable is also instrumental in the characterization of the indentation point of other materials, such as Shop Tube 2 (blue), which have a negative score and coherently display a smoother and more delayed indentation.

  The fifth latent variable grows for:

  - higher tensile stiffness of the material
  - lower tube diameters

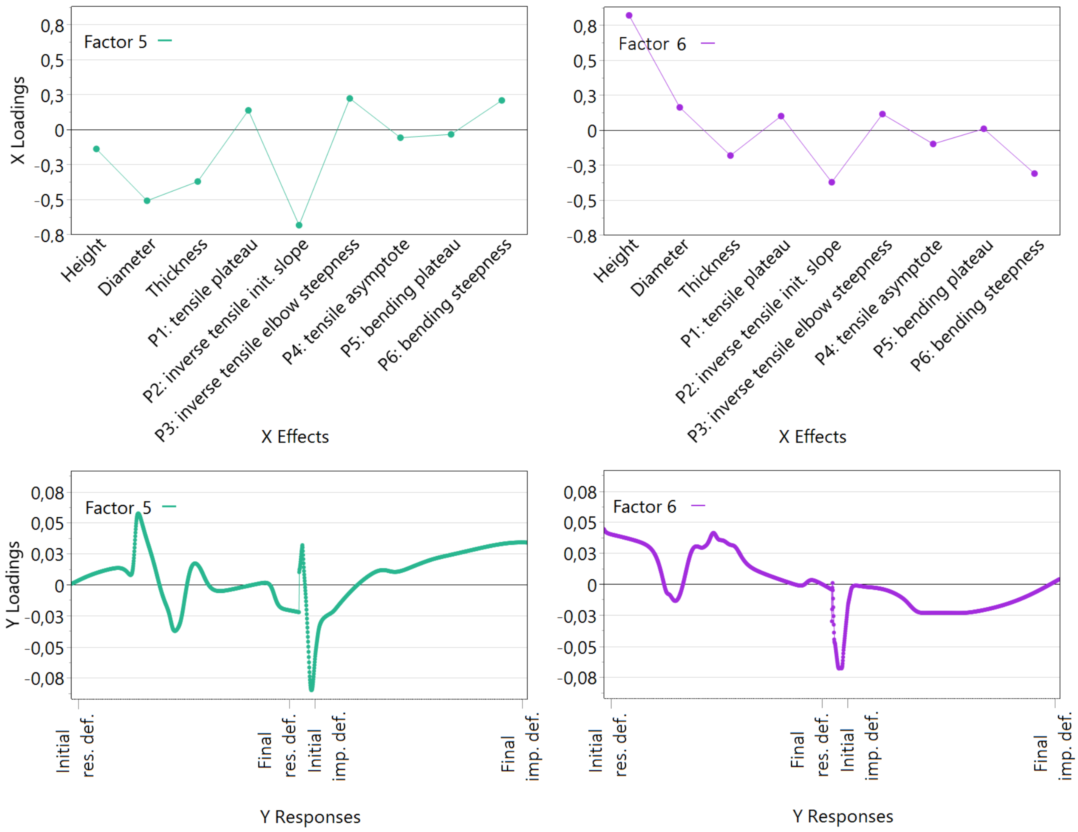


Figure 3.36. *Predictors and responses loading plots for the latent variables 5 and 6 of the PLS model.*

– lower tube thicknesses

The key learning is that tube denting will be more sudden and sharp for tubes composed of materials with high tensile stiffness, but also in the case of thinner materials or for lower tube diameters.

Such conclusions are coherent with respect to what is observed practically and experimentally.

These observations are to some degree redundant with respect to what was observed from previous latent variables, nonetheless, they offer a slightly different insight regarding the impact of tensile stiffness and are particularly useful in modellistic terms, the capture the behavior of some deviating observations.

- **Latent variable 6:** by studying the loadings it can be concluded that the sixth latent variable correlates tube height with a greater initial slope of the denting curve. The scores confirm this interpretation. In practical terms this means that higher tubes are more prone to retain slight deformations; considering that small deformations are hardly noticeable, they are not considered a defect, thus this latent variable is of little interest in the study of the denting phenomenon. Moreover, in quantitative terms, the effect is so marginal that it could almost be neglected.

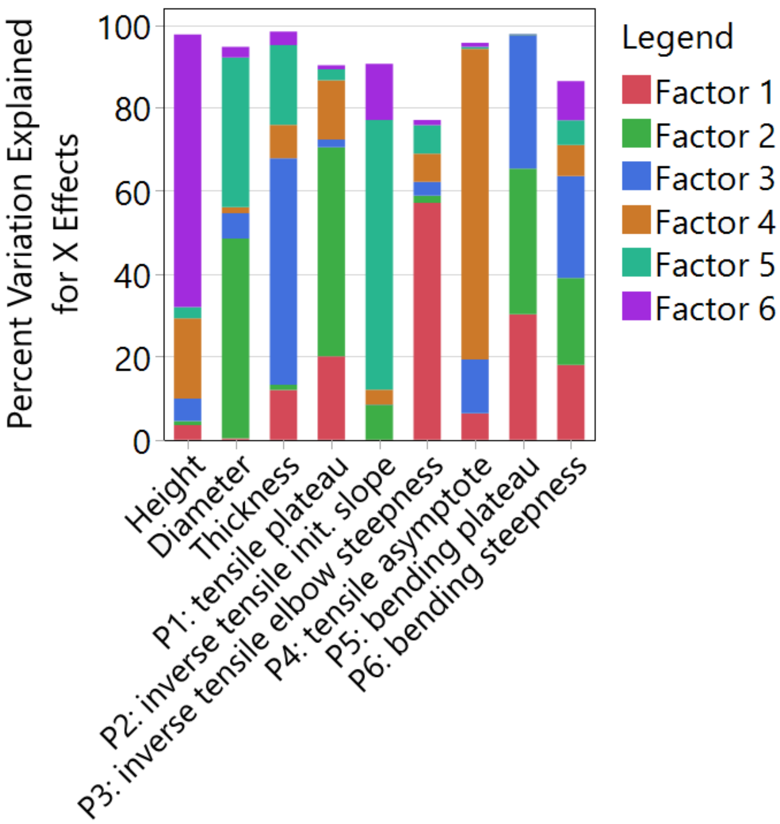


Figure 3.37. *Percentage of the predictors variability explained by each latent variable of the PLS model.*

It is worth noting that latent variables 4, 5, and 6 only account for a small fraction of the dataset variability, this means that they are only marginally relevant and have more of a "corrective" function (often related to peculiarities of a few samples) instead of defining the overall trend of the denting curve (as the first three latent variables).

3.5.4.4 Model diagnostics

The meaningfulness of the regression model is confirmed through a series of observations:

- observing the predictors vs responses score plots (Figure 3.33 it can be verified that a linear model structure is adequate;
- the cumulative R^2 statistic reaches adequately high values both regarding the predictors and the responses, indicating once again that the linear modelling methodology is adequate and that the majority of the data variability can be explained by the correlation structure;
- all terms of the regression model can be interpreted, meaning that they are meaningful, namely they are related to real phenomena taking place during tube denting, and can be thus be relied on for performing predictions. In other terms, the latent variables do not just fit noise.

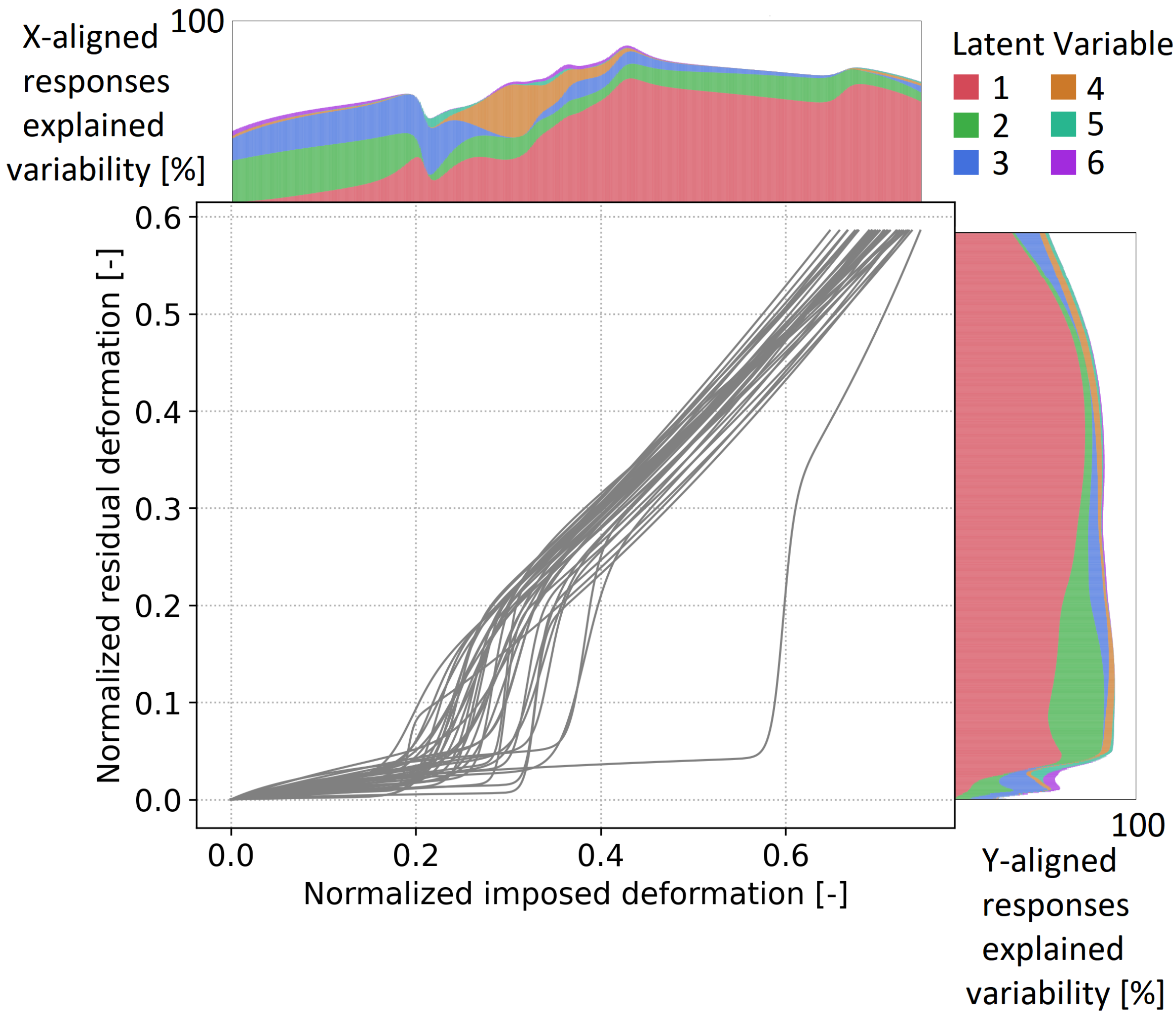


Figure 3.38. *Percentage of the responses variability explained by each latent variable of the PLS model.*

Outlier analysis

It only remains to assess whether all observations used to develop the model can be considered appropriate. Observations are appropriate if they are sufficiently similar to each other to prove beneficial in model training (improving predictive capabilities). If an observation is markedly dissimilar from the others, its inclusion in the dataset might prove harmful to the model.

To adequately evaluate these aspects, the Hotelling's T^2 and Q statistics are studied (Figure 3.39 and 3.40).

The most problematic samples are without a doubt the ones corresponding with Shop Tube 3 and 4 (respectively highlighted in orange and purple in the plots). It was already observed (by performing a PCA on the predictors) that these materials are indeed peculiar (Figure 3.26); it can now be confirmed, in relation to a high value of the T^2 statistic, that also in terms of denting behavior they markedly differ from the rest of the samples (still within the correlation structure of the model). Details regarding the deviations from average behavior of these materials are reported in Section 3.5.4.3, during latent variables interpretation.

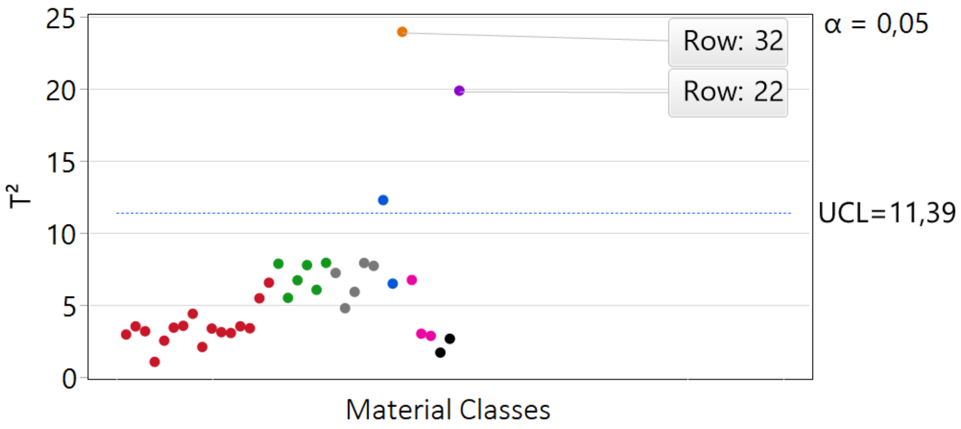


Figure 3.39. *Hotelling's T^2 statistic plot of the PLS model. Upper confidence limit fixed with respect to $\alpha = 0.05$. Colors distinguish the observations by material classes:* ***red****=HDPE/EVOH,* ***magenta****=HDPE/PET,* ***grey****=ABL,* ***green****=PP,* ***black****=Shop Tube 1,* ***blue****=Shop Tube 2,* ***orange****=Shop Tube 3,* ***purple****=Shop Tube 4. The identification numbers of the outliers refer to the "Run" values in Table 3.11.*

In terms of the Q statistic instead only two moderate outliers are identified:

- one observation regards a PP tube, whose denting measurement deviates slightly from the others (likely an experimental error);
- one observation regards Shop Tube 4, whose denting curves are notoriously different from the others.

Model boundaries regarding predictions on new materials

The fact that the variability of Shop Tube 3 can be caught by the model correlation structure is to be regarded with a certain degree of skepticism: while performing the PCA on the predictors (Section 3.5.1.1), it was concluded that the fitting function for the tensile mechanical data, while being completely adequate for polymeric materials, has too many parameters for materials containing cellulose, which are stiff and brittle and could basically be fit by a straight line. For this reasons, the parameters P1 and P3 of Shop Tube 3 do not reflect reality.

Considering that parameters P1 and P3 are of great importance for the model correlation structure, it follows that it is very likely that the good fit of the observation is more the result of a coincidence than of its adequacy. This is confirmed by the inconsistency of empirical observation with respect to the sample score for latent variable 1: recalling what was previously said, the model interprets the tube's behavior as related to a marked resistance to indentation, while in reality the sample dents quite readily.
All these considerations are enough to prove that the sample should be excluded from the calibration dataset for the sake of the model predictive performance.

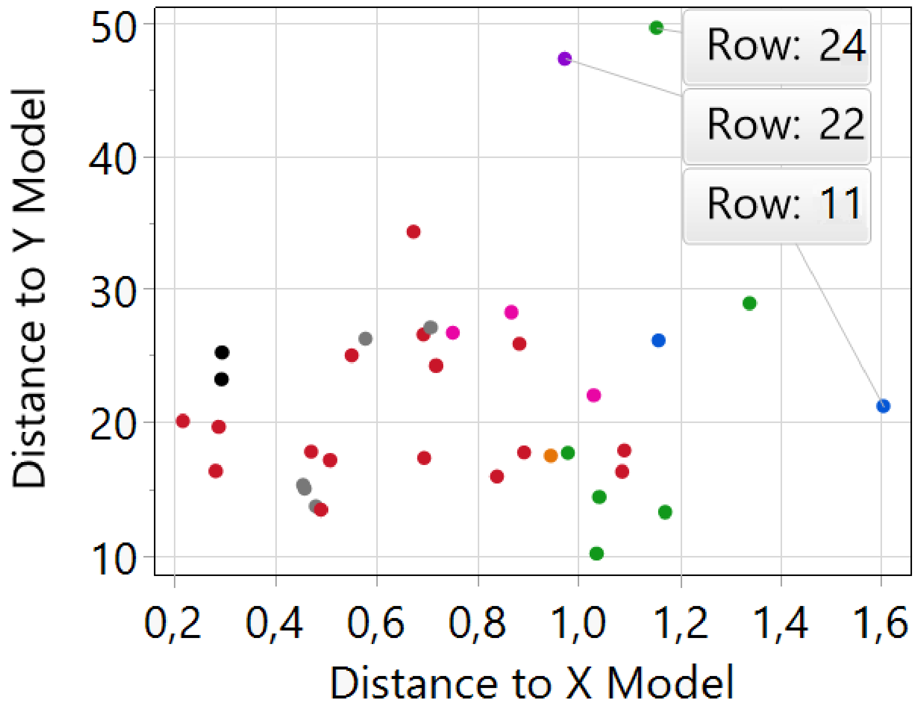


Figure 3.40. *Q statistics plot of the PLS model. Colors distinguish the observations by material classes:* ***red****=HDPE/EVOH,* ***magenta****=HDPE/PET,* ***grey****=ABL,* ***green****=PP,* ***black****=Shop Tube 1,* ***blue****=Shop Tube 2,* ***orange****=Shop Tube 3,* ***purple****=Shop Tube 4. The identification numbers of the outliers refer to the "Run" values in Table 3.11.*

The issue regards all tubes containing cellulosic material, for which the model's predictive capabilities should not be regarded as adequate. At this point in time, not enough cellulosic materials (for use in packaging tubes) are available to develop a reliable statistical model based exclusively on their data.

When they will be available, it will be possible to build a dedicated dataset and replicate the strategy described in this study, with the slight difference of using a simpler fitting function for the tensile data.

The development of a model capable of handling all tubes materials, regardless of the presence of cellulose, would be ideal. For this reason, the sample will be kept in the dataset in the following part of the study (to assess the model predictive capabilities also in its regards); this is done for the sake of experimentation, while for business studies and predictions, a model excluding Shop Tube 3 has been developed separately.

Nonetheless, the observations regarding the meaninglessness of parameters P1 and P3 for cellulosic materials remain an issue to be tackled if it is desired to develop a general model; a possible solution to be implemented in future studies could be to perform imposed deformation mechanical tests instead of imposed force tests. This could allow brittle materials to develop a more complete plateau without snapping and thus provide a better fit to the tensile parameters.

The limited capability of the model to describe Shop Tube 4 variability is also important to be discussed: the material is an outlier within the predictors dataset and coherently the tube is also an outlier within the responses, both in terms of T^2 and Q statistics; on a positive note, in terms of distance from the responses model (Q statistic), the tube is just a moderate outlier.
This means that there are features of the denting curve which the model is not able to account for within its structure, and regarding the features that the model can capture, the item presents extreme behaviors (very different from the average). These observations do not automatically constitute a problem, as long as the majority of the features of the curve are captured and interpreted correctly; this is the case for latent variable 1 (the indentation point is heavily shifted "to the right"), less so for latent variable 2 (the model suggests that the tube dents smoothly, while the denting is rather sharp).
After careful consideration it is concluded that the observation should be retained within the dataset: the marked influence it has on the model is regarded as beneficial, considering that the sample represents the only instance of a tube which is highly resistant to denting.

Model boundaries regarding tube geometry

The model has been trained on D40 and D50 tubes with heights ranging from 14 to 18.5cm; its reliability is thus only guaranteed within these ranges, even though, up to a moderate extent, predictions resulting from extrapolation could provide interesting insights (for instance regarding D60 tubes).

As a general rule regarding model boundaries, if the prediction of the denting curve is performed on a newly available tube, the T^2 statistic should be evaluated. If the metric crosses the threshold value, it is suggested to distrust the predictive capabilities of the model and instead to perform a denting test on the sample and to use the results to retrain the model.

Display of predictive capabilities

As a final assessment of the predictive capabilities of the PLS model, some denting curves are generated and displayed (Figure 3.41): when using the complete dataset to train the model, the predictions performed on the calibration dataset are clearly quite accurate (such predictions are referred to as *modelled* and are displayed in red in the figure); in such cases the NRMSE between measured and modelled curves never surpasses 6%, and is on average 2.5%. If cross-validation is instead performed (training the model on datasets that exclude one by one the fourteen materials), the predictions slightly worsen, but are still reliable; Shop Tubes 3 and 4 are exceptions and the associated prediction dramatically worsens when their data is excluded from the dataset. Nonetheless, given that such samples represent outliers within the dataset, this is expected. All things considered, the results obtained from performing cross-validation on Shop Tube 4 are on the contrary rather encouraging, showing that the model is capable of predicting the tube's notable denting resistance regardless of its highly peculiar mechanical properties (even though in reality the tube performs even better). The NRMSE between measured and predicted (cross-validation) denting curves has its maximum at 18.3% and is on average 5%.

3.5.4.5 Considerations regarding model inversion

Given the notable degree of explained variability that the model displays relatively to the predictors dataset, it is reasonable to think of the possibility of model inversion.
This is an open route for future investigations, in fact, it would be possible to design an optimal denting curve and to use the inversed model to identify the most desirable material properties for tube denting resistance.

3.6 Denting Index comparison diagram

The last achievement presented in this work is the delivery of a tool to easily compare tubes in terms of denting performance. In fact, denting curves contain a lot of information and might not be readily interpretable to the inexperienced user; consequently, it is desirable to be able to express the denting performance of a tube in a more simple way. This issue can be solved by identifying a scalar value that rates each tube in terms of its performance.

3.6.1 Definition of denting index

In order to obtain a single scalar which represents the denting propensity of the item, it is possible to proceed either arbitrarily, identifying a feature that captures the phenomenon of interest (like the inflection point in a denting curve) or it is possible to use mathematical methods, for instance, by leveraging the knowledge acquired in the previous sections, using the scores of a latent variable from the PLS model.

The first of the two approaches is recommended only in the case in which, thanks to prior knowledge, it is proven that the chosen feature is sufficient to capture adequately the phenomenon. Considering that the method to characterize denting here described is innovative, no prior knowledge is available. Thus the statistical approach (based on a sufficiently wide set of denting curves) is to be preferred.
The first latent variable proves perfect for the purpose: not only it explains the greatest amount of variability among all, but it is proved that it is directly related to the capability of the tube to resist greater imposed deformation without denting. It thus precisely quantifies the denting resistance of the tube. It follows that the denting index of a tube will be defined as the value of the score of the first latent variable (from the PLS model developed on a representative set of tubes).
A disadvantage of using statistical methods to obtain a denting index is that the value corre-

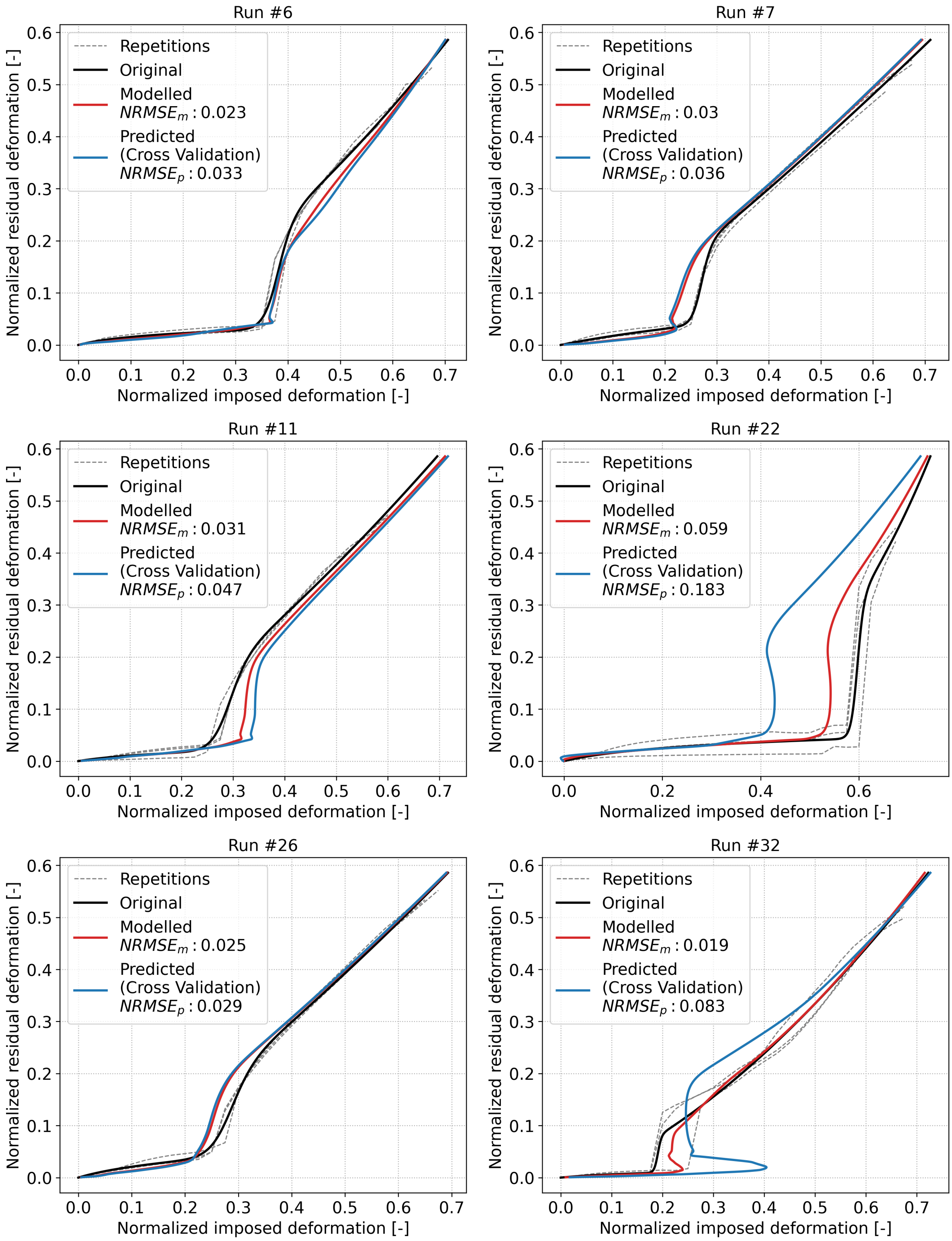


Figure 3.41. *Showcase of the predictive capabilities of the PLS model, highlighting some average cases (runs 6, 7, 11, and 26) and some difficult cases (runs 22 and 32). Difficult cases correspond to outliers, thus the model performance is worse in cross-validation and gets better when including the sample in the dataset. To identify the features of the tubes corresponding to each run refer to Table 3.11.*

sponding to a specific tube is not absolute, namely, with just one curve available this approach cannot be used; it instead depends on the set of available denting curves and thus in a way on the values of the denting index of all the other studied tubes. This means that each time the model is retrained (changing the dataset) the value of the denting index of each tube will slightly change. Nonetheless, considering the notable variety of tubes in the calibration dataset, it is expected that changes in the value of the denting index will not be substantial, even upon retraining of the model.

3.6.2 Threshold value for the denting index

Based on the definition of the denting index, the lower its value, the worse the denting resistance of the tube is. A threshold needs to be set, under which a tube denting performance is not acceptable. From empirical knowledge and observations, it is broadly accepted among the company's experts that the denting performance of ABL tubes is inadequate. With regard to this observation, the threshold value for the denting index can be set equal to the highest score of ABL tubes; two different thresholds are defined for D40 and D50 tubes (respectively with values of -17 and -37), considering that a different denting performance is expected from each diameter format.

3.6.3 Denting Index predictions

In Figure 3.42 a diagram comparing denting indices is displayed; for each material and tube diameter, the diagram contains:

- the values of the denting index corresponding to:
  - the measured denting curves (*measured*);
  - the predicted denting curves when the material is included in the calibration dataset (*modelled*);
  - the predicted denting curves when the material is not included in the calibration dataset (*predicted*).
- the error (averaged among body heights):
  - between *measured* and *modelled* denting index;
  - between *measured* and *predicted* denting index.

The error is normalized with respect to the range of the denting index (relative error).

It is worth noting that:

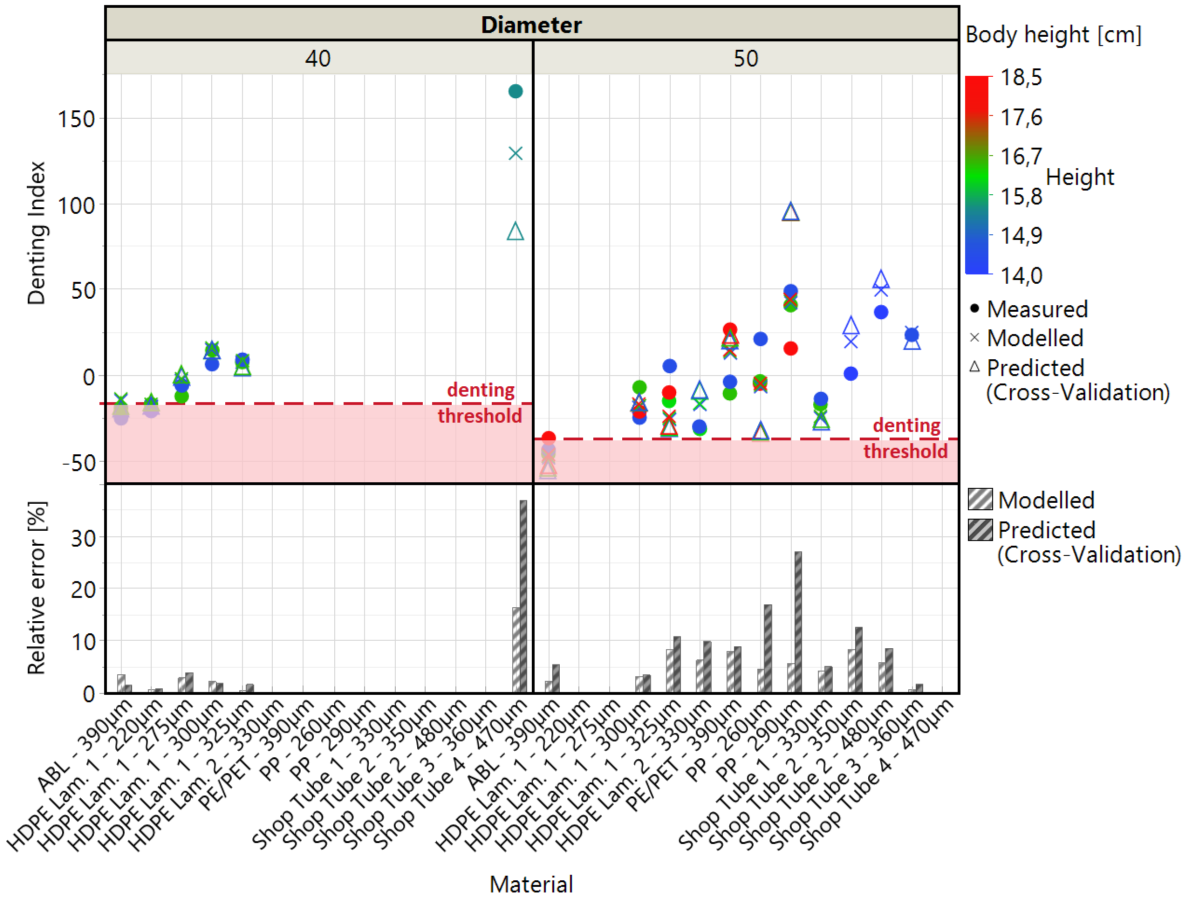


Figure 3.42. *"Measured", "modelled" and "predicted" denting indices, evaluated for the available combinations of tube diameter, body height, and material; the height-averaged relative error of* modelled *and* predicted *denting indices is also displayed in the form of a bar plot.*

- all tested materials have a better (or equal in the case of HDPE Lam. 1 - 220µm) performance than ABL tubes; this isn't surprising, as it is well known that ABL tubes have the worst denting performance in the group; it is instead a useful as a reference point to quantify other tubes' performance;

- as discussed in the previous sections, the denting index corresponding to Shop Tube 3 is not representative of its denting behavior. This highlights the limitations of the model in regard to the characterization of cellulose composites;

- the relative error in the prediction of the denting index of Shop Tube 4 (cross-validation) is considerable (36%); this is in line with the fact that the material is an outlier and thus the prediction proves to be a hard task for the model. Nonetheless, the prediction is on the right track and is greatly enhanced by including the material in the dataset (the error associated with the *modelled* denting index is reduced to 16%);

- the mean height-averaged relative error across all materials and diameters is 9.1% for *predicted* denting indices and 4.7% for *modelled* denting indices. This is regarded as a good result, which confirms the tool reliability for the prediction of tube denting performance.

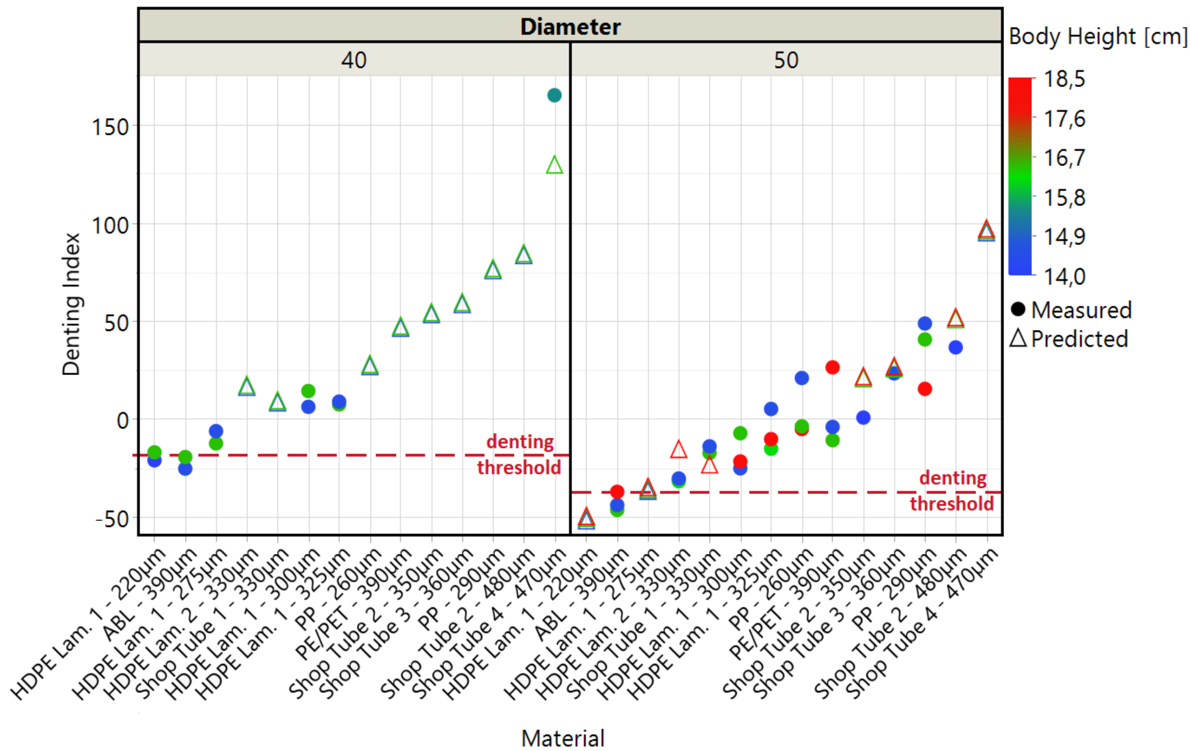


Figure 3.43. *"Measured" and "predicted" denting indices, respectively for available and non-available combinations of tube diameter, height, and material.*

The denting index has been predicted for all tubes corresponding to combinations of height and diameter for which it was not possible to produce a sample. The results are shown in Figure 3.43. The predictions are coherent with the expectation, with the only noteworthy observation that a D50 tube composed of HDPE Lam. 1 - 220µm has an even worse denting performance than ABL. This is easily explained given the thinness of the material, which was never used for manufacturing D50 tubes for this exact reason.

3.6.4 Impact of tube geometry, material and wall thickness

The denting index diagram can be used to quantify the impact of individual factors on the denting performance of tubes, without having to access the metrics of the PLS model:

- the tube **diameter** has a significant impact on tubes, worsening their performance by around 30 points when going from D40 to D50;
- the tube **body height** has a negligible impact on denting, this was first discussed during the interpretation of the model's latent variables (Section 3.5.4.3) and can be also observed in the *measured* values of the denting index: the three values corresponding to each material and diameter do not appear in a specific order, and their succession is related to chance (experimental errors);

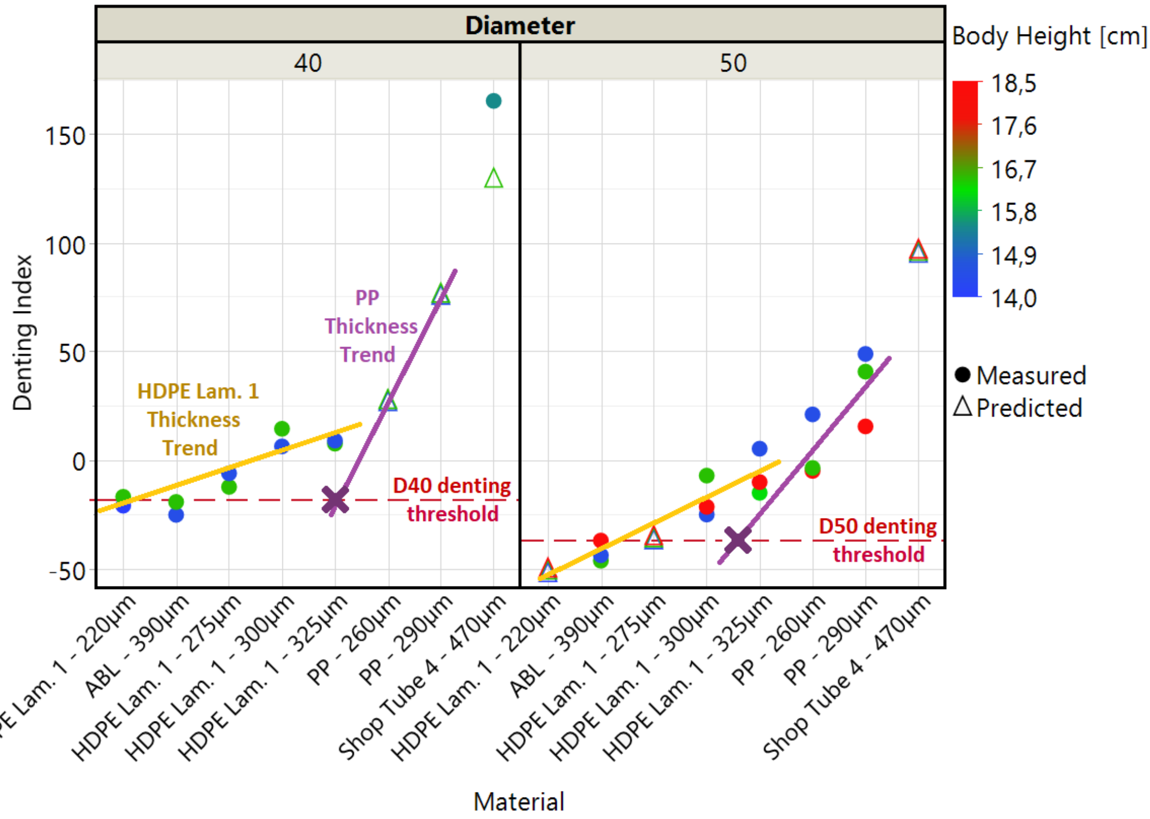


Figure 3.44. *Denting index diagram highlighting the correlation between the index value and the thickness of materials belonging to the same class.*

- a linear trend can be observed between the denting index and the **thickness** of materials belonging to the same group. This is clearly presented in Figure 3.44.

  Such a trend is extremely useful since it provides (through either interpolation or extrapolation) a qualitative indication of the material thickness that would be optimal to achieve a denting performance close but still superior to the threshold value.

  Two examples of such applications are:

  - the yellow trend line in Figure 3.44 can be used to interpolate the optimal thickness for D50 tubes made of HDPE Lam. 1, which is around 250µm;
  - the purple trend line in Figure 3.44 can be used to extrapolate the optimal thickness for D50 tubes made of PP, which is around 220µm.

Conclusions

The project achieved its goals and can thus be regarded as successful:

- a quantitative test method for tube denting performance was proposed to be used in place of the formerly employed qualitative evaluations; such a method proved useful as a means to measure the response variables of the predictive model, but has the potential to be used on its own, to compare denting performance of available tubes;
- a reliable predictive model was developed to evaluate the denting performance of tubes from the mechanical properties of their constituent material.

Nevertheless, in order to allow for a conscious use of the model, it is also important to acknowledge the limitations of the study:

- it doesn't explore the effect on tube denting performance of important factors such as temperature and fill level; such variables are known to have a marked influence on denting performance and are subject to regional variations; they should therefore be investigated to a greater extent in future studies;
- the model has some inherent flaws when it comes to predicting the denting behavior of tubes containing cellulosic materials; this is related to the markedly stiff nature of such materials, which makes inadequate the fitting functions and parameters commonly used for polymeric materials. Nonetheless, solutions to these issues are proposed for future studies, such as:
  - performing imposed-deformation tests instead of imposed-force tests to measure tensile properties of the samples; this would aid stiffer materials in developing a plateau, at least to some degree, which would in turn provide more accurate coefficients from the fitting of the data through the currently employed functions, and thus generate better predictors for model development;
  - developing a stand-alone model for cellulosic composite materials, adjusting coherently the fitting function for tensile data.

On the path towards the study's goals, software tools and data management techniques were devised; specifically:

- within the field of data management:
  - a two-parameters logistic function has been proved to provide a good fit to bending tests data sourced from a broad variety of tube material samples;

  - a modified four-parameters Hill's equation has been proved to provide a good fit to tensile tests data sourced from a broad variety of tube material samples;
  - multiple datasets formulations for predictive modelling (combinations of different formats of predictors and responses) have been developed; particular efforts were made to identify options that maintained all the valuable information initially contained in the raw data, even though the tests data of different materials (predictors) or tubes (responses) often ranged in different intervals.

- all the above-mentioned data treatments can be performed automatically, thanks to the development of Python scripts that turn the raw data directly into datasets (software tools).

Such techniques have the potential to be reimplemented in similar circumstances to the ones that led to their development.

Last but not least, all the factors which can influence tube performance (in general terms) were detailed; among them, through statistical Design of Experiment, the most influential with regard to denting performance have been proven to be the mechanical properties of the material (including its thickness), tube diameter, and tube body height.
This narrowing of the factors allowed to focus the experimental campaign on a broad set of materials and tubes; consequently, the resulting dataset proved adequate to implement multivariate modelling techniques (such as PLS) and to develop a precise understanding of the mechanisms through which the key variables influence the denting of tubes; the main conclusions regarding the phenomena at the basis of denting are the following:

- The insurgence of the indentation is discouraged in materials which slowly transition to a plastic behavior and possess a high yield strength; these dependencies are coherent with the expectations, given that they tend to prevent the concentration of the stresses in "weak points", which would yield (leading to the indentation), and instead help the tube structure in holding and deforming as a whole.

- The promptness of the indentation is heavily dependent on tube diameter: greater diameters are related to a greater initial tolerance to small deformations but are also bound to a more sudden indentation. Also material properties play a role, with materials with a higher yield strength and bending stiffness being once again more resilient to small imposed deformations and then suddenly yielding.

This knowledge will undoubtedly prove useful in future developments and studies regarding packaging tubes performance.

Nomenclature

Acronyms

ABL	=	Alluminium Barrier Layer
CBL	=	Ceramic Barrier Layer
CV	=	Coefficient of Variation
DMA	=	Dynamic Mechanical Analyzer
DoE	=	Design of Experiment
EVOH	=	Ethylene Vinyl Alcohol
HDPE	=	High Density Polyethylene
MPD	=	Materials, Process & Delivery
NRMSE	=	Normalized Root Mean Squared Error
PBL	=	Plastic Barrier Layer
PCA	=	Pricipal Component Analysis
PCR	=	Pricipal Component Regression
PLS	=	Partial Least Square Regression
PP	=	Polypropylene
RMSE	=	Root Mean Squared Error
RRMSE	=	Relative Root Mean Squared Error

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Acknowledgements

I would like to express my sincere gratitude to my supervisor Prof. Carlo Boaretti and my co-supervisor Prof. Pierantonio Facco for constantly and readily assisting me for the whole duration of the project.

Furthermore, I would like to show my appreciation to my company supervisor Christian Schneider for being a constant reference point when in need of technical help or suggestions, as well as an example of thoughtfulness (and patience).

I would also like to thank all my ex-colleagues within the Hair Care Packaging MPD team. In particular, Chiara Pagliuca and Sven Seibert. I've really appreciated the opportunity of spending these months at your side, learning from your suggestions, and sharing cheerful moments with you.

Finally, I would like to thank my family and friends for all their continued support over the years and in the toughest moments.