THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

Development of a model to predict the mechanical properties of adhesives based on the formulation

by

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ABSTRACT

In order to contribute to the development of research in the field of adhesives for the footwear industry, this study aimed to develop mixed numerical-experimental models aiming to predict and optimize the mechanical properties of adhesives using their weight compositions as design variables.

In this work polyurethane solvent based adhesives were considered. The characteristics and properties that polyurethane polymers, resins and additives confer to the adhesive were determined. For evaluation and control of the resultant mechanical properties, the most common tests used by the footwear industry were performed. These are the peel strength and the creep rate.

In the literature, it's possible to find several works based on adhesives, specifically about their composition. However, there are no studies regarding the mathematical models to optimize polyurethane solvent based adhesive formulations.

In this type of adhesives, it is necessary to take into consideration that there are factors which determine the efficiency of the adhesive joints, such as the type of substrates that are to be bonded and the surface treatment. Thus, for the implementation of this work, the following materials were considered: natural leather for the upper, polyurethane (PU) and thermoplastic rubber (TR) for the soles. Chemical and physical treatments were applied, such as halogenation and mechanical carding, respectively.

Therefore, the design variables were the constituent materials of the formulation of the polyurethane solvent based adhesive. The single-objective or the multi-objective optimization techniques were applied aiming to determine optimal adhesive formulations, improving in these ways the efficiency of the adhesive joints. The models were built using Genetic Algorithms supported by Artificial Neural Networks and Global Sensitivity Analysis concepts.

From this research it was concluded that it is possible to build mixed numerical-experimental models aiming to predict and optimize the mechanical properties of adhesive joints. The models show robustness and capability to solve a wide variety of problems in footwear industry.

RESUMO

No sentido de contribuir para o desenvolvimento da investigação na área dos adesivos para a indústria do calçado, este trabalho teve como objectivo a determinação de modelos híbridos numéricos e experimentais capazes de prever e optimizar as propriedades mecânicas das juntas adesivas usando as composições dos constituintes como variáveis de projecto.

Neste trabalho foram considerados adesivos de poliuretano de base solvente, sendo determinadas experimentalmente as características e influências que os polímeros de poliuretano, resinas e aditivos conferem ao produto adesivo. Na indústria do calçado, as propriedades mecânicas controladas são a resistência ao arrancamento e a resistência à temperatura. Deste modo, foram aplicadas como técnicas a força de arrancamento e a taxa de fluência.

Na literatura, é possível encontrar vários trabalhos sobre adesivos, mais concretamente sobre a sua composição. No entanto, não existem pesquisas no que se refere a modelos matemáticos capazes de optimizar formulações de adesivos de poliuretano à base de solvente.

Neste tipo de adesivos, há que ter em conta a existência de factores que determinam a eficiência das juntas adesivas, como é o caso do tipo de substratos que se pretendem colar e os tratamentos de superfície necessários para a obtenção da junta adesiva ideal. Assim sendo, para a execução deste trabalho, foram considerados os materiais seguintes: pele natural, solas de poliuretano (PU) e solas de borracha termoplástica (TR). Foram aplicados tratamentos químicos e físicos, nomeadamente a halogenação e a cardagem mecânica.

Deste modo, as variáveis de projecto foram as matérias-primas constituintes da formulação do adesivo de poliuretano à base de solvente. As técnicas de optimização com um único objectivo ou com multi-objectivos foram aplicadas com o intuito de determinar formulações óptimas, melhorando desta forma a eficiência das juntas adesivas. Os modelos foram construídos usando

Algoritmos Genéticos apoiados por conceitos de redes neurais artificiais e de análise global de sensibilidade.

A partir desta investigação concluiu-se que é possível construir modelos híbridos numéricos e experimentais com o objectivo de prever e optimizar as propriedades mecânicas de juntas adesivas. Os modelos mostram robustez e capacidade para resolver uma ampla variedade de problemas na indústria do calçado.

ACKNOWLEDGEMENTS

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A special thanks to my co-supervisor Prof. Carlos A.C. António for the involvement in my work and for sharing his knowledge with me about the optimization using Artificial Neuronal Network (ANN) and Genetic Algorithm (GA) in Fortran.

I would like to thank to all my colleagues at **ADFEUP** group, Ricardo Carbas, Mariana Banea, Ana Queirós, Filipe Chaves for the friendship and for interesting discussions about adhesives. A special thanks to Eduardo Marques for the contributions made to this work.

During my work in **FEUP**, I had the support of the company ***CIPADE – Indústria e Investigação e Desenvolvimento de Produtos Adesivos, S.A.*** where I work since 2003; I want to acknowledge them because they understood my efforts and choices in these three years.

I would like to thank to my friends and colleagues for their friendship and moral support.

Finally, I would like to thank to my family, especially my daughter that was born during this project, for their unconditional love, patience and support, that made possible the realization of this work.

This thesis is dedicated to the memory of my brother (Marco Paiva).

CONTENTS

LIST OF PUBLICATIONS

[1] Paiva, R.M.M.P, Marques, A.S.E., da Silva, L.F.M., Antonio, C.A.C, Arán-Ais F., **Adhesives in the footwear industry**, *Journal of Materials: Design and Applications,* **0(0)**, 1-18 (2015).

[2] Paiva, R.M.M., Marques, E.A.S, da Silva, L.F.M., Vaz, M.A.P., **Importance of the surface treatment in the peeling strength of joints for the shoes industry**, *Applied Adhesion Science*, **1(5)**, 1-15 (2013).

[3] Paiva, R.M.M.P, Marques, A.S.E., da Silva, L.F.M., Antonio, C.A.C., **Surface Treatment effect in Thermoplastic Rubber and Natural Leather for the footwear industry**, *Materials Science and Engineering Technology,* **46(6)**, 632-643 (2015).

[4] Paiva, R.M.M.P, Marques, A.S.E., da Silva, L.F.M., Antonio, C.A.C., **Effect Of The Surface Treatment In Polyurethane And Natural Leather For The Footwear Industry**, *Materials Science and Engineering Technology,* **46(1)**, 47-58 (2015).

[5] Paiva, R.M.M., Antonio, C.A.C., da Silva, L.F.M., **Sensitivity and optimization of peel strength based on composition of adhesives for footwear**, *The Journal of Adhesion*, **91(10-11)**: 801-822 (2014).

[6] Paiva, R.M.M., Antonio, C.A.C., da Silva, L.F.M., **Optimal design of adhesive composition in footwear industry based on creep rate minimization**, *The International Journal Advanced Manufacturing Technology*, accepted (2015).

[7] Paiva, R.M.M., Antonio, C.A.C., da Silva, L.F.M., **Multiobjective optimization of mechanical properties based on the composition of adhesives**, *International Journal of Mechanics and Materials in Design,* accepted (2015).

GLOSSARY

ABS – Acrylonitrile Butadiene Styrene

ANN – Artificial Neural Networks

CR – Creep Rate

EVA – Vinyl Acetate Ethylenic

FTIR – Fourier Transform Infrared Spectroscopy

GA – Genetic Algorithm

GSA – Global Sensitivity Analysis

MDO – Multi-objective Design Optimization

PA – Polyamide

PS – Peel Strength

PU – Polyurethane

PVC – Polyvinyl Chloride

SEM – Scanning Electron Microscope

SA – Sensitivity Analysis

SBR – Styrene Butadiene Rubber

TPU – thermoplastic polyurethane

TR – Thermoplastic Rubber

SUMMARY OF THESIS

1. INTRODUCTION

1.1. Motivation

Adhesives have a performance which varies with their composition [1-2]. In the footwear industry there is a high requirement on adhesives, which must be adjusted to the materials used by manufacturers in different collections for each season [3-4]. A large variety of materials is usually employed in the construction of the shoe [3]. For each new adhesive there is also a huge pressure to achieve good results in short-term. However the development process can require hours of research in search for scientific knowledge which does not always result in obtaining, in a short-term, formulations with good results. Therefore, the determination of the right adhesive must increasingly be a more effective process, concluded in the shortest time as possible.

1.2. Problem definition

This project goal is to determine a mathematical model capable of predicting the mechanical properties of a particular formulation, thereby allowing the minimization of the response time to identify needs in the footwear industry, also minimizing the resources necessary for such development. The design variables are the weight percentages of the solid raw material constituents of the adhesive, such as polyurethanes (PUs), resins and additives. The PUs are resins thermoplastics and resins are thermorigid types [5-7]. In the selection of the adhesive, several factors must be taken into account such as the type of substrates to be bonded and the surface treatments necessary to obtain the optimum adhesive joint [8-12]. For the implementation of this work, the following materials were considered: natural leather, soles of polyurethane (PU) and thermoplastic rubber soles (TR). Chemical and physical treatments were applied, such as halogenation and mechanical carding, respectively [13-14]. To optimize the adhesive formulation, the Genetic Algorithm (GA) was considered [15-16].

1.3. Objective

The objective is to develop a methodology capable of innovating the process of research and development of adhesives in footwear industry. In other words, the main task of this work is the definition of optimization strategies to develop new products, seeking to optimize response times and thereby increasing the effectiveness of the adhesive formulations. This is reflected in an increase in competitiveness of the adhesive producer.

Specific objectives are:

- Constrained minimization of the creep rate,
- Constrained maximization of the peel strength.
- Multi-objective optimization for constrained maximum peel strength and minimum creep rate

1.4. Research methodology

The following methodology was adopted to achieve the goals of this PhD research, as shows the Figure 1.

To understand the importance of the adhesive in the footwear industry, a review was carried out, describing the process steps for the shoes manufacturer, with the adhesives involved defined in **Paper 1** [1-4].

In **Paper 2**, **Paper 3** and **Paper 4**, in order to understand the importance of surface treatments on the materials to be joined, tests were accomplished to verify the impact on the relevant mechanical properties for the shoe industry, in particular on the peel strength [9-12], [17]. The standard EN ISO 20344:2004, EN 1392:1998 and EN 15307:2007 was taken into account whenever possible [18].

According to the information gathered during the literature review, the most demanding adhesive joint in the manufacturing process of the shoe is the bonding of the upper to the sole [3-4].

In **Paper 5** and **Paper 6** the Taguchi method, Artificial Neural Networks (ANN) and Genetic Algorithms (GA) was applied to each of the studied mechanical properties (peel strength and creep rate) [15-21]. A mono-objective method was applied to obtain an optimal solution [15]. A FORTRAN programming language was used in Artificial Neural Networks (ANN) and Genetic Algorithms (GA).

When considering the two properties simultaneously, peel strength and creep rate, the numerical model was developed as multi-objective, this improved model being presented in **Paper 7** [16].

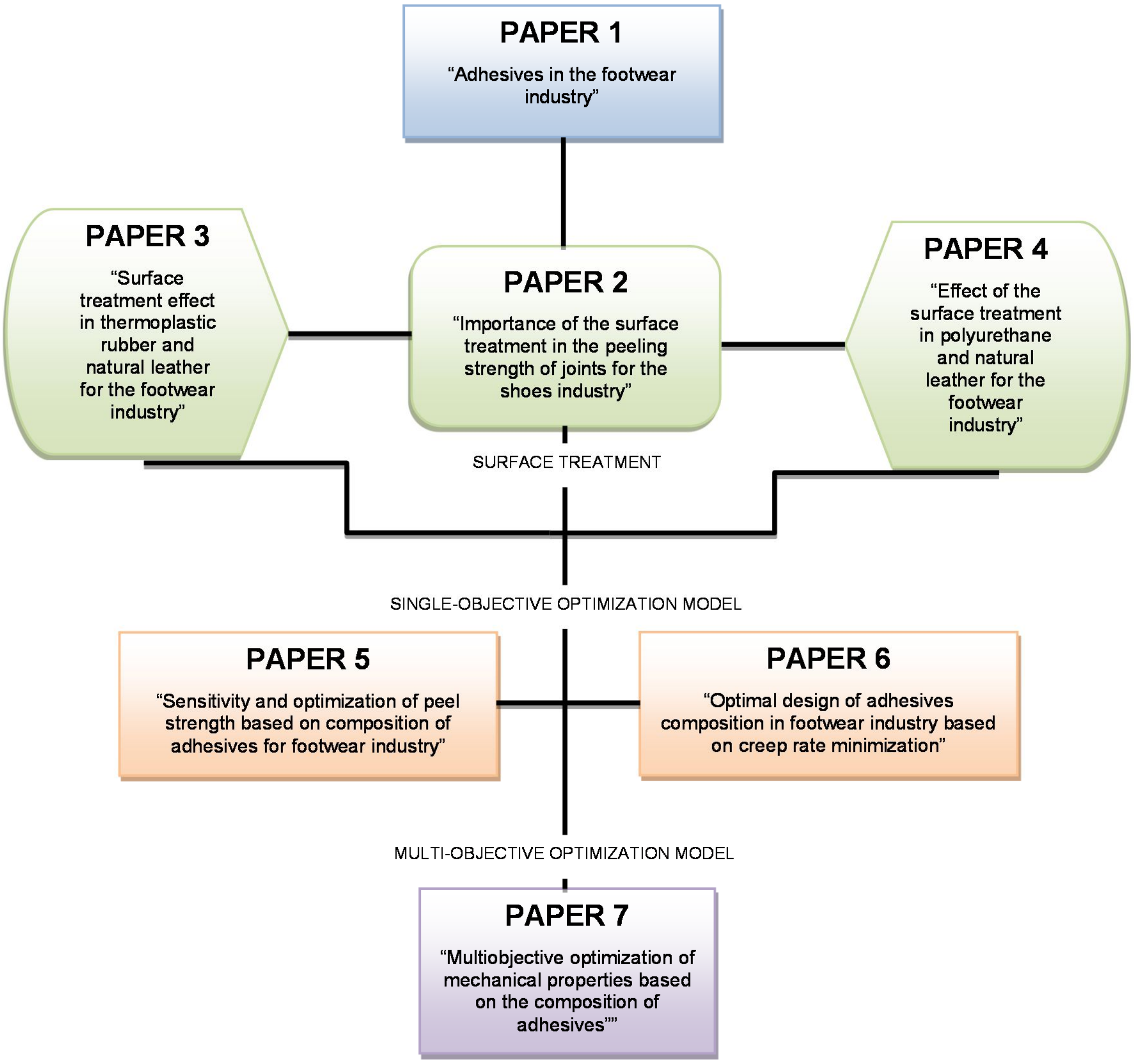

Figure 1: Methodology adopted in this PhD research

1.5. Outline of the thesis

This thesis consists of seven appended papers:

PAPER 1

Paiva, R.M.M.P, Marques, A.S.E., da Silva, L.F.M., Antonio, C.A.C., Arán-Ais F., **Adhesives in the footwear industry**, *Journal of Materials: Design and Applications*, **0(0)**, 1-18 (2015).
DOI:10.1177/1464420715602441

ABSTRACT

Footwear manufacturing is basically a process of transformation and assembly of various components made up of several materials where different adhesives play a key role, because without them, the shoe would lack of shape and structure. This paper aims to understand the importance of adhesives in the footwear industry. It is necessary to identify the different processes in a shoemaking where adhesives are involved and the different adhesive joints produced, as well as their technical requirements. The adhesive joint performance will depend on the different adherends nature used as footwear materials, the joint design, the surface treatments, the adhesive properties which depend on their formulation, etc.

Adhesive joints in a shoe acts under different stress types (peel, shear, tensile, etc). The most desfavourable are the peel stress. For that reason the peel strength test is one of the most common to evaluate adhesive joints performance. When heat resistance is an important adhesive requirements, a creep test is carried out. Furthermore, aging tests are undertaken in order to evaluate durability. This methodology is described in this paper.

In the literature, one can find several papers on adhesives, specifically on their mechanical properties. However, there is little research related to footwear applications, including not only the mechanical properties that this industry demands but also the composition of the adhesives.

ABSTRACT

Therefore, this paper aims to connect the important mechanical properties for the footwear industry with the constituents of the adhesives. However, other properties are also important, such as viscosity, wettability, compatibility, etc, depending on the materials and the adhesive joint type.

PAPER 2

Paiva, R.M.M., Marques, E.A.S, Silva, L.F.M., Vaz, M.A.P., **Importance of the surface treatment in the peeling strength of joints for the shoes industry**, *Applied Adhesion Science* **1(5)**, 1-15 (2013).
DOI:10.1186/2196-4351-1-5

ABSTRACT

In order to contribute to the research and development of adhesives for the shoe industry, this paper aims to analyze the peel strength of an adhesive joint with various types of surface treatments. In the shoe industry, the adhesive properties are very important to ensure the quality of manufacture of the shoe, thus, to better understand the behaviour of the adhesive joint, it is important to analyze the peel resistance in order to adjust the manufacturing process. For the execution of this work, we considered the following materials: natural leather, thermoplastic rubber (TR), polyurethane (PU) and a polyurethane non structural adhesive solvent based. This paper analyzes the influences of the application of chemical and / or physical surface treatments on substrates in the peel strength of a T joint. It was found that certain surface treatments, depending on the substrate, are required to obtain an adhesive joint capable of satisfying the minimum required by the shoes sector.

PAPER 3

Paiva, R.M.M.P, Marques, A.S.E., da Silva, L.F.M., Antonio, C.A.C., **Surface Treatment effect in Thermoplastic Rubber and Natural Leather for the footwear industry**, *Materials Science and Engineering Technology,* **46(6)**, 632-643 (2015).
DOI: 10.1002/mawe.201500403

ABSTRACT

This paper aims to analyze the peel strength of an adhesive joint with various types of surface treatments. In the shoe industry, the adhesive properties are very important to ensure the quality of manufacture of the shoe, thus, to better understand the behaviour of the adhesive joint, it is important to analyze the peel resistance in order to adjust the manufacturing process. In this work, natural leather, thermoplastic rubber (TR) and a non-structural, solvent based, polyurethane adhesive were considered. The influence of the application of chemical and / or mechanical surface treatments on substrates in the peel strength of a T joint were analysed. To characterize the surfaces, several test were considered, including Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscope (SEM) and contact angle measurements. It was found that certain surface treatments are required to obtain an adhesive joint capable of satisfying the minimum strength requirements of the shoes sector.

PAPER 4

Paiva, R.M.M.P, Marques, A.S.E., da Silva, L.F.M., Antonio, C.A.C., **Effect Of The Surface Treatment In Polyurethane And Natural Leather For The Footwear Industry**, *Materials Science and Engineering Technology,* **46(1)**, 47-58 (2015).

DOI: 10.1002/mawe.201400277

ABSTRACT

The aim of this paper is to analyze the peel strength of an adhesive joint with various types of surface treatments in order to contribute to the research and development of adhesives for the footwear industry. In the shoe industry, the adhesive properties are very important to ensure the quality of manufacture of the shoe. To better understand the behavior of the adhesive joint, it is important to measure the peel resistance of the adhesive and use it to adjust the manufacturing process. For this work, joints were manufactured using natural leather, polyurethane (PU) and a solvent based polyurethane non structural adhesive. The influences of the application of physical surface treatments and/or primer on substrates in the peel strength of a T joint were analyzed. Several tests were used to characterize the surfaces of the substrates, including Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscope (SEM) and contact angle measurements. It was found that certain surface treatments are required to obtain an adhesive joint capable of satisfying the minimum requirements of the shoes manufacturing sector.

PAPER 5

Paiva, R.M.M., Antonio, C.A.C., da Silva, L.F.M., **Sensitivity and optimization of peel strength based on composition of adhesives for footwear**, *The Journal of Adhesion*, **91(10-11)**: 801-822 (2014).
DOI: 10.1080/00218464.2014.971119

ABSTRACT

In order to contribute to the research and development of adhesives for the footwear industry, this paper aims to develop a model capable to predict and optimize the peel strength from the composition of adhesives. The proposed approach is based on three stages: experimental planning of measurements, global sensitivity analysis for uncertainty propagation and optimization procedure. The design variables are the weight percentages of the solid raw material constituents such as polyurethane, resins and additives of the adhesive joint.

Considering the experimental results obtained for Taguchi design points as input/output patterns, an Artificial Neural Network (ANN) is developed based on supervised evolutionary learning. Using the developed ANN a global sensitivity analysis procedure is implemented and the variability of the structural response of adhesive joint is studied. The optimal solution for adhesives composition for maximum peel strength is investigated based on ANN model and using a Genetic Algorithm. The proposed approach is able to predict the optimal peel strength including its sensitivity to uncertainties. The results show that the sensitivities of design variables belonging to polyurethane and additive groups are important for optimal adhesive joint. The optimal peel strength based on proposed approach is consistent with the experimental testing data.

PAPER 6

Paiva, R.M.M., Antonio, C.A.C., da Silva, L.F.M., **Optimal design of adhesive composition in footwear industry based on creep rate minimization**, *The International Journal Advanced Manufacturing Technology*, accepted (2015).

ABSTRACT

On the footwear industry the composition of adhesives have a high contribute for the product quality. This paper aims to develop a model capable to predict and optimize the creep rate using the composition of the adhesive joints. The proposed mixed numerical and experimental approach is based on following stages: the planned experimental measurements; the learning procedure aiming to obtain the optimal artificial neural network (ANN) configuration; and the optimal design procedure for adhesive joint composition. The design variables are the weight percentages of the solid raw material constituents of the adhesive, such as polyurethanes (PUs), resins and additives.

Considering the experimental results obtained for Taguchi design points as input/output patterns, the ANN is developed based on supervised evolutionary learning. In the last stage the optimal solution for adhesives composition considering minimum creep rate is investigated based on ANN and genetic algorithm. The optimal results for creep rate minimization based on proposed approach are reached when large quantities for PUs and for some additives are considered, and when colophony and vinyl resin aren't considered on the formulation.

The sensitivity of the structural response of footwear adhesives to composition constituents is also studied based on Sobol indices obtained from ANN-Monte Carlo simulation procedure. The performance measured by creep rate of the adhesive joint is very sensitive to the influence of some polyurethanes and a particular sensitivity to caprolactone types with extremely high crystallization is observed. The sensitivities of the creep rate to the resins Colophony and Coumarone-Indene are also important.

PAPER 7

Paiva, R.M.M., Antonio, C.A.C., Silva, L.F.M., **Multiobjective optimization of mechanical properties based on the composition of adhesives,** *International Journal of Mechanics and Materials in Design,* accepted (2015).

DOI:10.1007/s10999-015-9313-2

ABSTRACT

A mixed numerical-experimental approach capable to predict and optimize the performance of the footwear adhesive joints, based on the weight composition of used raw materials was presented. The approach based on the optimal design of adhesive composition to achieve the targets of minimum creep rate (CR) and maximum peel strength (PS) under manufacturing. Two stages are considered in the proposed approach. In the first stage, an approximation model is built based on planned experimental measurements and artificial neural network (ANN) developments. The ANN learning procedure uses a genetic algorithm. In the second stage an optimal design procedure is developed based on multi-objective design optimization (MDO) concepts. The MDO algorithm based on dominance concepts and evolutionary search is proposed aiming to build the optimal Pareto front. The model uses the optimal ANN to evaluate the fitness functions of the optimization problem. Furthermore, a ANN-based Monte Carlo simulation procedure is implemented and the sensitivity of the creep rate and peel strength relatively to weight compositions of raw materials is determined.

The approach shown robustness to establish the trade-off between minimum creep rate properties and minimum inverse peel strength (maximum peel strength) using the weight composition of used raw materials. The optimal results for both CR and PS based on proposed approach are reached when large quantities for polyurethanes (PUs) and for some additives are considered. The performances of adhesive joints measured by CR and PS are very sensitive to the influence of some PUs and in some way are moderately sensitive to additives. The proposed MDO approach supported by experimental tests shows improved explorative properties of raw materials and can be a powerfully tool for the designers of adhesive joints in footwear industry.

2. ADHESIVES TESTED

This thesis studied one type of adhesive: Solvent based PU adhesives.

However, the formulation of this type of adhesive varies depending on the raw materials considered in Table 1, and the constraints as shown in Table 2.

Table 1: Raw-materials used in adhesive formulation and Taguchi levels definition.

Materials		% weight on formula	Levels
PU's:			
1.	**Caprolactone with extremely high crystallization**	0-20	1/2/3
2.	**Polyester with extremely high crystallization**	0-20	1/2/3
3.	**Polyester with very high cryistallization**	0-20	1/2/3
Resins:			
4.	**Colophony WW**	0-1	1/2/3
5.	**Hydrocarbon (C9)**	0-1	1/2/3
6.	**Alkyl phenolic**	0-1	1/2/3
7.	**Terpene phenolic**	0-1	1/2/3
8.	**Coumarone-Indene**	0-1	1/2/3
9.	**Vinyl Chloride / Acetate Vinyl**	0-1	1/2/3
Additives:			
10.	**Fumaric Acid**	0-0.6	1/2/3
11.	**Hydrophobic silica**	0-2	1/2/3
12.	**Nitrocellulose**	0-2	1/2/3
13.	**Chlorinated rubber**	0-3	1/2/3

Table 2: Constraints used in adhesive joint optimization definition.

Constraints	% weight on formula
Total % PU	10-20
Total % Resins	0-1
Total % Additives	0-7

The Taguchi design points were used to plan the adhesive experiments. 27 experimental data sets were selected inside the interval domain of each design (random) variable and levels defined in Table 1. Each one of these 27 design points corresponds to an adhesive formulation.

The Taguchi values were selected according to the approach proposed by Taguchi and Konishi [15]. By the selected Taguchi table L27(3^{13}) the actual composition for each Taguchi design point is obtained, as shown in Table 3.

Table 3: Taguchi design points: % weight on formulation (design variables values).

Design point	Design variables (raw-materials)												
	1	2	3	4	5	6	7	8	9	10	11	12	13
1	2.5	2.5	2.5	0	0	0	0	0	0	0	0	0	0
2	2.5	2.5	2.5	0	0.2	0.2	0.2	0.2	0.2	0.3	1	1	1.5
3	2.5	2.5	2.5	0	0.5	0.5	0.5	0.5	0.5	0.6	2	2	3
4	2.5	5	5	0.2	0	0	0	0.2	0.2	0.3	2	2	3
5	2.5	5	5	0.2	0.2	0.2	0.2	0.5	0.5	0.6	0	0	0
6	2.5	5	5	0.2	0.5	0.5	0.5	0	0	0	1	1	1.5
7	2.5	10	10	0.5	0	0	0	0.5	0.5	0.6	1	1	1.5
8	2.5	10	10	0.5	0.2	0.2	0.2	0	0	0	2	2	3
9	2.5	10	10	0.5	0.5	0.5	0.5	0.2	0.2	0.3	0	0	0
10	5	2.5	5	0.5	0	0.2	0.5	0	0.2	0.6	0	1	3
11	5	2.5	5	0.5	0.2	0.5	0	0.2	0.5	0	1	2	0
12	5	2.5	5	0.5	0.5	0	0.2	0.5	0	0.3	2	0	1.5
13	5	5	10	0	0	0.2	0.5	0.2	0.5	0	2	0	1.5
14	5	5	10	0	0.2	0.5	0	0.5	0	0.3	0	1	3
15	5	5	10	0	0.5	0	0.2	0	0.2	0.6	1	2	0
16	5	10	2.5	0.2	0	0.2	0.5	0.5	0	0.3	1	2	0
17	5	10	2.5	0.2	0.2	0.5	0	0	0.2	0.6	2	0	1.5
18	5	10	2.5	0.2	0.5	0	0.2	0.2	0.5	0	0	1	3
19	10	2.5	10	0.2	0	0.5	0.2	0	0.5	0.3	0	2	1.5
20	10	2.5	10	0.2	0.2	0	0.5	0.2	0	0.6	1	0	3
21	10	2.5	10	0.2	0.5	0.2	0	0.5	0.2	0	2	1	0
22	10	5	2.5	0.5	0	0.5	0.2	0.2	0	0.6	2	1	0
23	10	5	2.5	0.5	0.2	0	0.5	0.5	0.2	0	0	2	1.5
24	10	5	2.5	0.5	0.5	0.2	0	0	0.5	0.3	1	0	3
25	10	10	5	0	0	0.5	0.2	0.5	0.2	0	1	0	3
26	10	10	5	0	0.2	0	0.5	0	0.5	0.3	2	1	0
27	10	10	5	0	0.5	0.2	0	0.2	0	0.6	1	2	1.5

The numerical model was determined considering the 27 different adhesives and the mechanical properties peel strength and creep rate, experimentally obtained.

3. EXPERIMENTAL TESTS

The most common tests used by the footwear industry are the peel strength and the creep rate. These standard properties are described on the EN 1392:1998.

3.1. Peel Strength

In this thesis, for the manufacture of the joint, smaller peel specimens were used.

The adhesive joint studied was composed of two substrates (150mm x 30mm) bonded together in an area of 100mm x 30mm, as shown in Figure 2.

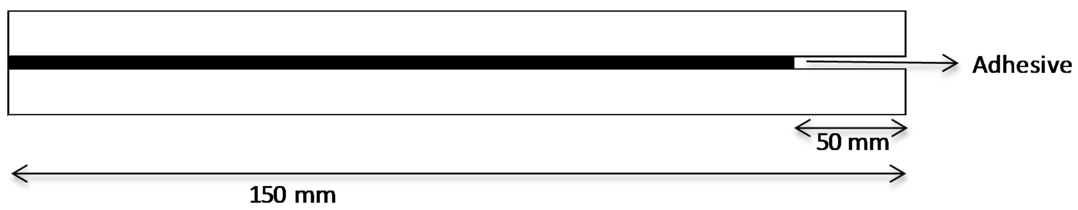

Figure 2 – Test piece geometry

To guarantee the cure, 24 hours after the manufacture of the adhesive joint, the peel test was performed in the testing machine at a speed of 50 mm/min. The results are expressed as load versus displacement (N/mm).

This test was used in **Papers 2-5** and **7**.

3.2. Creep Rate

The creep rate is a property which determines the temperature resistance of the single lap joint. Creep rate is a variation of displacement per unit of time, under a constant load in a constant high temperature.

The adhesive joints, were stored in standard conditions (23 °C and 50% RH) during 72h, in order to ensure the complete cure of the adhesive [17-18].

In this thesis smaller creep specimens were considered to manufacture the adhesive joint, composed of two substrates (150mm x 30mm) bonded together in an area of 100mm x 30mm, as shown in Figure 2.

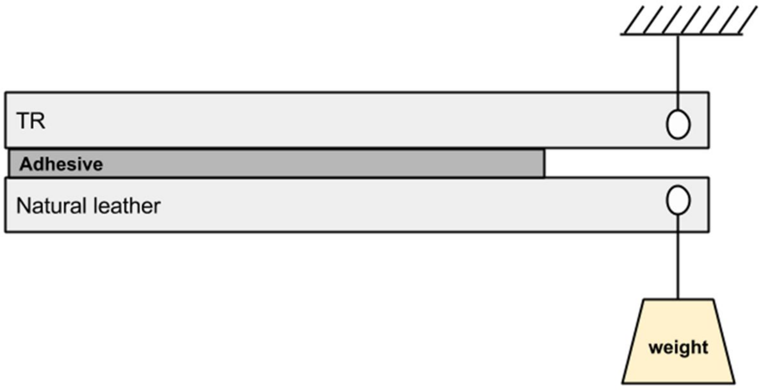

Figure 3. Test piece geometry and adhesive joint for creep test.

The creep test was performed in the heat activator at 60 °C. The specimen was loaded with the specified constant weight (1,5 kg).

The cabinet of the heat activator was opened periodically and the separations (in mm) of the bonds substrates were marked while still loaded. The time (in min) to complete separation [21] is recorded. A “creep failure envelope” was obtained with the creep experiments that can be divided into three phases: primary, secondary and tertiary. The primary phase corresponds to an instantaneous elastic strain, the secondary phase corresponds to a constant creep rate and the tertiary phase happens with the failure of the specimen [4, 17-18].

In calculating the mean of the separation lengths of the bond the primary and the tertiary phases were ignored [4]. The results are expressed as displacement (millimetres, mm) versus time (minutes, min).

This test was used in **Papers 6** and **7**.

4. NUMERICAL MODELING

The first column of the proposed optimization strategy is the definition and construction of the physical model representing the adhesive joint of footwear product and the relationship between the design variables – the weight composition of raw materials, and the inherent structural response measured by creep rate and peel strength. The proposed approach for this first column is based on planned experimental measurements and using these testing results to develop the approximation model. First of all, the set of experiments are planned using the Taguchi method aiming to obtain a good coverage of the design space for the composition of the adhesive joint. Secondly, considering the experimental results obtained for Taguchi design points as input/output patterns, an Artificial Neural Network (ANN) is developed based on supervised evolutionary learning [21-23]. This ANN learning procedure is equivalent to solve an optimization problem where the difference between the experimental results and the ones obtained from the ANN is minimized controlling the ANN parameters.

At the end of each ANN optimal configurations search, three ANN-based Monte Carlo simulation procedures are implemented aiming to study the sensitivity of the structural response of adhesive joint relatively to input parameters/design variables. In particular the Sobol indices for global sensitivity analysis are used to establish the relative importance of the input parameters/design variables on the structural response measures [23-24]

4.1. Artificial Neuronal Network (ANN)

The Artificial Neural Network (ANN) is a nonlinear dynamic modeling system inspired by our understanding and abstraction on the biological structure of the human brain. Its architecture and operating procedures are based on a large number of highly interconnected processing units denoted by neurons and the linkages are similar to the brain synapses as in biological sense. The operating procedures include attributes such as learning, thinking, memorizing, remembering, rationalizing and problem solving [24].

In the ANN developments a weight value is associated with each synaptic connection between processing units that is defined as the connection importance. The weight value acts as a multiplicative filter together with the activation procedure performed by an appropriated function. The ANN architecture is formed by several layers of neurons and different matrices with synaptic weights can be identified as linkage elements between layers.

Learning of ANN occurs while modification of connection weight matrix is undertaken at the learning process. From examples of a phenomenon with particular behavior and following an appropriate learning rule the ANN acquires knowledge or relationship embedded in the input/output data. The ANNs are robust models having properties of universal approximation, parallel distributed processing, learning, adaptive behaviour and can be applied to multivariate systems [24, 21].

In this work three ANN numerical models are formulated from mathematical point of view. The three implementations are based on FORTRAN programming language followed by testing and validation as well. All ANN models consider the weight composition of raw materials of the adhesive joint, such as PU's, resins and additives as input parameters/design variables. However, the three ANN models have different output parameters/ response variables that imply diverse topological structures. The first ANN model has the peel strength as output variable, the second has the creep rate as output variable and the third has both creep rate and peel strength as output response variable.

All the proposed ANN models are organized into three layers of nodes (neurons): input, hidden and output layers. The synapses between input and hidden nodes and between hidden and output nodes are associated with weighted connections that establish the relationship between input data and output data. Deviations on neurons belonging to hidden and output layers are also considered in the proposed ANN models.

In the developed ANN models, the input data vector is defined by a set of experimental values for design/input variables, which are the weight composition of raw materials of the adhesive joint, such as PU's, resins and additives as referred. The procedures to build the ANN approximation models begin defining the set of planned experiments based on Taguchi method. Then, the experimental input/output patterns are used in *learning procedures* aiming to obtain the optimal ANN configurations [21, 24].

The *ANN learning procedure* is equivalent to solve an optimization problem based on minimization of the differences between the experimental results and the simulation values obtained from the ANN. In this optimization process the weights of synapses and the biases in neurons are used as design variables. So, detailing the process the optimal configuration of ANN is obtained minimizing the error between the simulated network outputs and the experimental data for creep rate (CR) or / and the peel strength (*PS*). The minimization of ANN *learning procedure* is performed using single Genetic Algorithms with appropriated genetic parameters.

4.2. Sensitivity Analysis (SA)

The study of the influence of the weight composition of raw materials on the structural response of adhesive joint is performed based on the Global Sensitivity Analysis (GSA) supported by variance-based methods [20, 22-26]. The creep rate, *CR* and the peel strength, *PS* are considered as measures of structural response of the adhesive joint. On other words, the objective is to measure and to rank the importance of the variability of design variables - the weight percentages of PUs, resins and additives in the adhesive composition, on the structural response of adhesive joint measured by creep rate, *CR* and the peel strength, *PS*.

Lets consider β_j the response functional, denoting the creep rate or the peel strength. Assuming that the variables are independent, the variance of the conditional expectation $var(E\langle\beta_j \mid x_i\rangle)$ is used as an indicator of the importance of the design variable x_i on the variance of β_j. This indicator is directly proportional to the importance of x_i. In particular, the first-order global sensitivity index of Sobol [18-19, 29-31] is used in normalized format.

In this work, the first-order global sensitivity index of Sobol is calculated using the Monte Carlo simulations method together Artificial Neural Network (ANN). So, the GSA is implemented using the optimal network configuration obtained at the end of each ANN learning procedure. Thus, is possible to avoid the exhaustive and costly experimental tests to obtain the variability of the input variables structural on response. The methodology to obtain the first-order global sensitivity index of Sobol is based on the algorithm proposed by António and Hofbauer [20, 23].

5. OPTIMIZATION FRAMEWORK

In this thesis the optimization problem was treated using the concept of the three pillars ("three-columns-concept") integrated into the optimization process and defined as follows:

First column: The physical model of the structure or phenomena;

Second column: The optimization algorithm;

Third column: The optimization model.

The **physical model** of the structure or phenomena is a physical model of the problem, which is the mathematical representation of the physical behavior of the structure/phenomena. To make such characterization, the state variables were identified, obtaining the objective functions and constraints, allowing the creation of the representative model, for that were used as procedure the Artificial Neural Networks (ANN). Here, the first column of the proposed optimization strategy is the definition and construction of the physical model representing the adhesive joint of footwear product and the relationship between the design variables – the weight composition of raw materials, and the inherent structural response measured by creep rate and peel strength. The proposed approach for this first column is based on planned experimental measurements and using these testing results to develop the ANN approximation model.

The **optimization algorithm** operates as a search facility to obtain the optimal solution. There are several methods for this optimization. In this study the global optimal search technique and the method of evolutionary research were considered. This last technique made use of a Genetic Algorithm (GA), based on the law of survival of the species ("Darwin's theory").

The **optimization model** is the operational bridge between the physical model and the optimization algorithm. Here it is defined the architecture of optimization model connecting the different modulus collecting data necessary for optimization algorithm which comes from the optimization problem formulation. So, it allows determining the values of the objective functions and constraints from the state variables. For this purpose, any strategy of decomposition or the application of dominance concepts in multi-objective optimization for example, are defined this third column.

Generally it can be said that the structure of the model that follows the concept of the three pillars to optimize a problem started by determining the parameters that vary during the optimization process, followed by the creation of an optimal model to describe the mathematical relationship between the state variables and the design variables, ending up with the model validation that determined the values of the objective function and constraints from the state variables.

The single-objective or the multi-objective optimization techniques are applied aiming to determine an optimal adhesive formulation, improving in these ways the efficiency of the adhesive joints manufactured in the footwear industry.

5.1. Single-Objective Optimization

In the first single-objective design optimization procedure the optimal solution for adhesives composition for maximum peel strength is searched. The structural response of adhesive joint is measured by peel strength *PS*, calculated using the optimal ANN configuration. The design variables is denoted by vector **x**, which components are the weight percentages of PUs, resins and additives in the adhesive composition. The mathematical formulation of the optimization problem of adhesive joint is defined as peel strength maximization subject to technological constraints as follows,

$$\text{Maximize}\quad \text{PS}(\mathbf{x})\ ,\quad \text{over}\quad \mathbf{x}\ , \tag{1}$$

subject to:

$$10 \le \sum_{k=1}^{n} x_k \le 20 \tag{2}$$

$$\sum_{k=1}^{r} x_{n+k} \le 1 \tag{3}$$

$$\sum_{k=1}^{a} x_{r+k} \le 7 \tag{4}$$

$$x_k^l \le x_k \le x_k^u \quad , \quad k = 1, \cdots, n+r+a \tag{5}$$

where *n*, *r* and *a* are the number of materials of each group of PUs, resins and additives considered for the adhesive joint, respectively. Those numbers will be defined in design process. The constants x_k^l and x_k^u are the lower and upper bounds of design variable x_k, respectively.

The proposed optimization algorithm is based on two stages using two different populations evolving by a Genetic Algorithm (GA). In the first stage using the Taguchi design points the ANN-based on GA is developed. In this stage the GSA is implemented using the optimal configuration of ANN. During the second stage the peel strength, *PS* is maximized under the constraints of the optimization problem The fitness evaluation is based on optimal configuration of the ANN obtained at the first stage. The model is described in **Paper 5**.

In **Paper 5**, a Taguchi-ANN-GA approach predicting the sensitivity of the peel strength as function of the composition of formulation used in adhesive joints was presented. The results show the robustness of the model to measure the influence of the raw material constituents on peel strength, which plays an important role on the optimal design of the adhesive joints.

The numerical results presented in **Paper 5** show that the sensitivities of the design variables belonging to polyurethane and additives groups are important for optimal design of the adhesive joint. The optimal results obtained for peel strength based on proposed approach is consistent with the experimental testing data used to implement the model. The proposed two-stage ANN-GA optimization approach supported by experimental tests shows improved explorative properties of design space and can be a powerfully tool for the designers of adhesive joints in footwear industry. It can be concluded that the sensitivities of the design variables belonging to the resins' group are not important for the optimization process. On contrary, the sensitivities of the other groups are important.

In **second single-objective optimization model** described in **Paper 6**, the structural response of footwear adhesive joint is measured by creep rate (*CR*), which represents the objective function of the problem to be minimized.

Therefore, it is intended to develop a model capable to predict and minimize the creep rate depending on the raw materials used in the composition of the adhesive joint. These design variables are the weight percentages of PUs, resins and additives in the adhesive composition. The mathematical formulation of the optimization problem of adhesive joint is defined as creep rate constrained minimization as follows,

$$\text{Minimize } \; CR(\mathbf{x}) \; , \quad \text{over } \; \mathbf{x} \, , \tag{6}$$

subject to technological and size constraints defined from Equation (2) to Equation (5).

The proposed approach is based on mixed experimental-numerical procedures. The experimental data obtained in previous described procedure is fundamental to perform the optimization search. Two stages are identified in numerical part of the proposed approach. These two stages are: 1) the learning procedure aiming to obtain the optimal ANN configuration, which supports the relationship between raw materials and creep rate; and 2) the optimal design procedure based on the search for optimal adhesive joint composition. In these two stages of numerical part of the proposed approach two optimization sub-problems are solved using independent evolutionary searches such as Genetic Algorithms (GA).

The optimal results obtained for creep rate minimization based on proposed approach is consistent with the experimental testing data used to implement the model. Indeed, the creep rate is minimized when large quantities for PUs and for some additives are considered, and when colophony and vinyl resin aren't considered on the formulation.

The performance measured by creep rate of the adhesive joint is very sensitive to the influence of some polyurethanes and a particular sensitivity to caprolactone type with extremely high crystallization is observed. The sensitivities of the creep rate to the resins Colophony and Coumarone-Indene are also important as shown in **Paper 6**. Although the contribution of the additives is related with the improvement of mechanical behavior of PUs and resins, their influence on creep rate is shown through the sensitivity of Fumaric Acid. On contrary, the influence of Chlorinated rubber is not explained directly attempting to low creep rate sensitivity relatively to this material.

5.2. Multi-Objective Optimization

The multi-objective design optimization (MDO) is based on constrained minimization of objective functions. However, in the proposed approach the performance of structural response of the footwear adhesive joints is measured by creep rate (*CR*) and the peel strength (*PS*). Furthermore, the optimal design of adhesive joint is performed based on minimization of creep rate and maximization of peel strength. So, this design procedure must be formatted according the constrained minimization formulation. The minimization of inverse of peel strength (*1/PS*) is adopted as second objective function to overcome this apparent difficulty.

Therefore, it is intended to develop a model capable to predict and simultaneously minimize the creep rate and the inverse of peel strength depending on the weight percentage of raw materials used in the composition of the adhesive joint. These design variables denoted by vector **x** with components x_k, are the weight percentages of PUs, resins and additives in the adhesive composition. The mathematical formulation of the bi-objective optimization problem of adhesive joint is defined as creep rate and inverse of peel strength minimizations subject to technological constraints as follows,

$$\text{Minimize} \quad \left(f_1(\mathbf{x}), f_2(\mathbf{x}) \right), \quad \text{over} \quad \mathbf{x} \tag{7}$$

with $f_1(\mathbf{x}) = CR(\mathbf{x})$ and $f_2(\mathbf{x}) = \dfrac{1}{PS(\mathbf{x})}$

subject to technological and size constraints defined from Equation (2) to Equation (5).

A MDO problem, when considering conflicting objectives, in general, cannot find an optimal solution for all purposes. So a decrease of an objective function involves increasing the other. Thus, the evaluation of possible solutions passes through the concept of Pareto Dominance.

In this work, the MDO process evolution is based on a short population of solutions updated during the evolutionary search driven by the genetic algorithm. An elitist strategy is adopted at evolution of short population. Each solution in short population is ranked according its fitness value, which is related with the objective functions and the constraints of the problem. The trade-off between minimum creep rate and minimum inverse peel strength, depending on given size and technological constraints imposed on the weight composition of raw materials used in adhesive joint, is searched.

It can be established that designs with good fitness and satisfying the constraints have priority in the rank process. Although this is necessary for bi-objective optimization problem it is not essential to build the optimal Pareto front. Indeed, the Pareto front depends on the dominance concept, which is applied at enlarged population. Here, the short population is used as a nest where the good solutions are generated through the genetic algorithm based on an elitist strategy. At each generation the best solutions of short population are stored into an enlarged population based on dominance concepts. The global Pareto-optimal front is built at this enlarged population using the concept of Pareto dominance [27].

Paper 7 describes the proposed approach to solve MDO problem. At the end of the optimization process, the Pareto front representing the frontier of the trade-off between the minimum creep rate and minimum inverse peel strength (maximum peel strength) for footwear adhesive joints is obtained. The global dominance measured in enlarged population at end of optimal design procedure is used to trace the associated Pareto front. The performance of the proposed approach to search for Pareto front's solutions considering the MDO problem can be observed.

6. CONCLUSIONS

The objective of this research was to develop a model capable to predict mechanical properties (peel strength and creep rate) based on the formulation of the adhesives. **Paper 1** shows that adhesives have an important impact in the show industry.

To define the best surface treatment in same materials, it was concluded in **Paper 2** and **Paper 3** that to maximize the peel strength of the leather/TR joints it is necessary to apply chemical treatment on TR and mechanical treatment and primer on leather. However, if it wasn't applied primer, it was possible to minimize the number of operations in the manufacture of shoes, while still being capable of satisfying the minimum requirements for the sector.

With **Paper 2** and **Paper 4** it was concluded that to maximize the peel strength of the leather/PU joints it is necessary to apply mechanical treatment and primer on PU and on leather. However, if it wasn't applied primer on both materials, it was possible to minimize the number of operations in the manufacture of shoes, while still being capable of satisfying the minimum requirements for the sector.

Several adhesive formulations based on PU's, resins and additives were tested taking into consideration the Taguchi method allowing to obtain experimentally the mechanical properties.

Applying GA as optimization methods, mono-objective and multi-objective models were obtained.

In conclusion it was possible to obtain good results with this thesis, since the developed models exhibit low errors, less than 4%. Furthermore, it is clear that with this work the optimal creep rate and peel strength based on proposed approach is consistent with the experimental testing data.

In **Paper 5**, the Taguchi-ANN-GA approach predicts the sensitivity of the peel strength as function of the composition of adhesive formulation show the robustness of the model, which plays an important role on the optimal design of the adhesive joints.

The numerical results developed on **Paper 5** show that the sensitivities of the design variables belongs to PU's and additives groups.

In **Paper 6** the set of experiments, defined by the Taguchi method, allow to obtain a good representation of the physical phenomenon. And the optimal results for the creep rate minimization based on proposed approach are reached when large quantities for Pus, Coumarone-Indene and for some additives are considered, and when colophony isn't considered on the formulation.

The optimal design of adhesive composition to achieve the targets of minimum creep rate and minimum inverse peel strength (maximum peel strength) under manufacturing constraints is obtained on **Paper 7**. The numerical results developed on show that the performances of adhesive joints measured by creep rate and peel strength are very sensitive to the influence of some PUs and in some way are moderately sensitive to additives.

The optimal results corresponding to the two best trade-off solutions of the constrained bi-objective optimization problem solved using the proposed approach is consistent with the experimental testing data used to implement the model. Indeed, the creep rate and the inverse of peel strength are minimized when large quantities for PUs and for some quantities of additives are considered. In this case the resins` group is not important except the weight percentage of Vinyl. The best trade-off Pareto front solution corresponding to numerical values CR=0.011198 [mm/min], PS=7.985 [N/mm] is used for experimental validation. The values of the considered best trade-off solution are consistent with the experimental validation results as shown in **Paper 7**.

7. FUTURE WORK

This thesis proposed a numerical model capable to predict mechanical properties, the creep rate and the peel strength, with the best formulation of an adhesive obtained.

The next step should be to use different materials for the adherend materials used in soles and uppers.

The application of this model using water based adhesives would be an interesting future improvement, taking into account the legal industry obligations.

Create a tool that allows the prediction of the joint's mechanical properties, peel strength and creep rate, using only as input the adhesive formulation and composition.

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APPENDED PAPERS

PAPER 1

LITERATURE REVIEW

ADHESIVES IN THE FOOTWEAR INDUSTRY

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Abstract

Footwear manufacturing is basically a process of transformation and assembly of various components made up of several materials where different adhesives play a key role, because without them, the shoe would lack of shape and structure. This paper aims to understand the importance of adhesives in the footwear industry. It is necessary to identify the different processes in a shoemaking where adhesives are involved and the different adhesive joints produced, as well as their technical requirements. The adhesive joint performance will depend on the different adherends nature used as footwear materials, the joint design, the surface treatments, the adhesive properties which depend on their formulation, etc.

Adhesive joints in a shoe acts under different stress types (peel, shear, tensile, etc). The most desfavourable are the peel stress. For that reason the peel strength test is one of the most common to evaluate adhesive joints performance. When heat resistance is an important

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adhesive requirements, a creep test is carried out. Furthermore, aging tests are undertaken in order to evaluate durability. This methodology is described in this paper.

In the literature, one can find several papers on adhesives, specifically on their mechanical properties. However, there is little research related to footwear applications, including not only the mechanical properties that this industry demands but also the composition of the adhesives.

Therefore, this paper aims to connect the important mechanical properties for the footwear industry with the constituents of the adhesives. However, other properties are also important, such as viscosity, wettability, compatibility, etc, depending on the materials and the adhesive joint type.

Key-words

Footwear, adhesives, raw materials, surface treatments, single lap joint, mechanical properties, contact adhesives.

1. INTRODUCTION

Nowadays, the footwear industry has a close association to the adhesives industry, using bonding techniques to join the variety of materials employed in the manufacture of shoes [1-2]. To better understand the importance of adhesives in the footwear industry in respect to the manufacture process of the shoe, it is very important to consider the operations that make up the process and the selection of the materials [1-2]. In the shoes manufacturing industry there are several operations that use manual processing steps [1-2]. The shoes manufacture is divided in eight main operating processes: storaging, modeling, cutting, sewing, lasting, assembling, finishing and packaging [1].

A wide range of materials is used in shoe manufacturing, including natural and synthetic leather, plastics materials, rubber and synthetic fibres, and adhesives [2]. The adhesives used in this industry are varied and their producers are always developing new products, following closely the market demands mainly due to the introduction of new materials according to fashion trends [1]. During the course of this work the importance of adhesives in the shoe industry will be analysed and the properties and performance of different types of adhesives explained.

Each of these types of adhesive can be formulated with several substances that will provide different performance to the final adhesive, influencing the materials able to be joined, the application method, the surface treatment, the adhesion strength, the cohesive strength, the creep strength as well as the wetting, drying time and adhesive hazard classification [3]. This work will only focus on the substances in the composition of the solvent based adhesives that influence the type of materials to be joined, the peel strength and creep strength. Such adhesives can have in its constitution elastomers, resins, additives and solvents [4].

For the manufacture of an adhesive joint, one must take into account the materials which are intended to be joined, using this to identify the most appropriate type of adhesive and surface treatments, enabling the maximization of the join resistance and durability through the adhesive joint design, as well technical requirements for such joint [2, 5]. There are four types of treatment usually employed in the footwear industry: physical, chemical, primer and solvent [5].

The footwear industry currently uses a large diversity of materials and over time this has increased the challenges placed on the adhesives industry, since bonding dissimilar materials with good performance requires specially formulated adhesives. This performance is usually evaluated with two significant mechanical properties, which are the peel strength and the creep strength [4].

2. FOOTWEAR DESIGN AND MANUFACTURING

2.1. Footwear components

In the past several years the high quality footwear market has proved to be a sector with a high potential that has been growing [7].

The prime goal of footwear was to protect the feet but wear comfort is also one of the biggest current concerns taken into account during shoe design and the material selection. The aesthetic component is also extremely important [8-9] all of these concerns lead to a very careful selection of the materials employed for shoe manufacture. Obviously, price is also a main factor that must be balanced with all these concerns.

An item of footwear, commonly referred to as a shoe, follows a particular construction, as identified in Figure 1.

Even taking into account this universal construction, it is possible to create varied designs. According to this construction, the shoe is formed by two main parts: the upper and the sole, as identified in Figure 1 [10-11]. The upper is formed by the vamp (that covers the front of the foot, covering the toecap), the counter (that covers the back of the foot), and joined by the quarter (covering the foot side) [10-12]. The lining is a inner upper constituent. The sole (known as outsole when is made of one piece) is the underside of the shoe, comprising the insole, midsole, bottom filler and the heel, as shown in Figure 1. These components are usually produced outside of the footwear manufacturer, in proper equipment for this purpose [12].

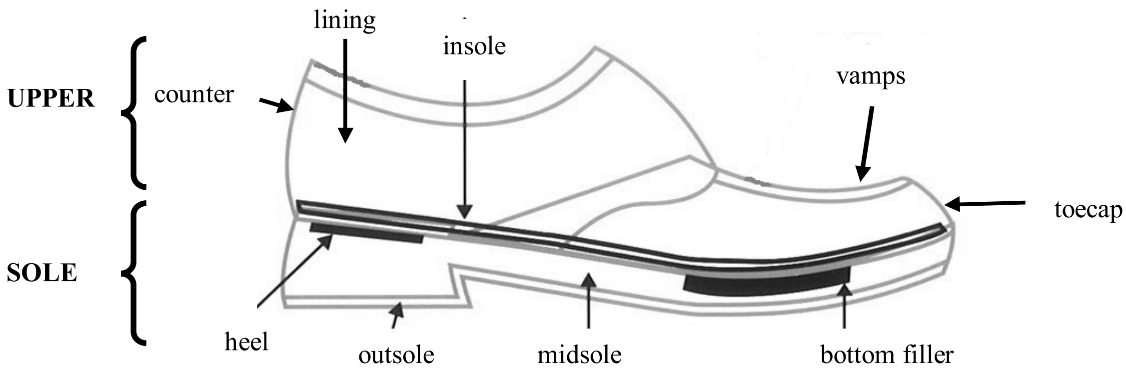


Figure 1: A typical construction of the shoe

2.2. Footwear classification and composition

In the footwear industry, independently of the type of materials used, to ensure its durability it is necessary for adhesive joints to fulfil certain specifications. Standard EN 15307 [6] establishes the minimum strength values recommended for footwear bonding. The peel strength values required for joining upper/sole, are shown in Table 1.

Table 1: Reference values of adhesion upper / soles, according to standard EN 15307

Shoes	Peel Strength per unit width (upper/sole)
infants footwear, indoor footwear, fashion footwear	≥ 2.5 N/mm
men town footwear, women town footwear, cold weather footwear, casual footwear	≥ 3.0 N/mm, or ≥ 2.5 N/mm with material failure
children footwear, general sports footwear	≥ 4.0 N/mm, or ≥ 3.0 N/mm with material failure
mountain footwear	≥ 5.0 N/mm, or ≥ 3.5 N/mm with material failure

2.3. Footwear materials

The quality and properties of the final product do not depend only on the correct execution of the shoemaking steps but also on the materials used during the construction. Therefore the material selection is crucial and one should take into account the technical performance, comfort environmental impact and economic aspect in the selection of materials. The material properties that influence the functional performance of the product that is being built should be the focus the material selection process. The applicability of a material is then determined by the ideal combination of properties, a combination capable to provide the best performance according to the desired performance standards. The selection of materials can be made taking into account several factors: the price, weight, size, ease of processing, durability, availability in the market, by mechanical, thermal, magnetic, physical, optical and electrical properties, or even by the environmental impact [3, 4]. Therefore, in the footwear industry, a wide variety of materials are used. The upper can be produced in polyvinyl chloride (PVC), natural or synthetic leather [4, 13], etc.

Performance requirements for uppers as footwear component, irrespective of the material, in order to assess the suitability for different end uses (sports, casual, men’s town, cold weather, women’s town, fashion, infants’ and indoor shoes) are established in the Technical Report ISO/TR 20879:2007 [14]. This report also establishes the test methods to be used to evaluate the compliance with requirements, including bondability, as described in Table 1.

The outsoles can be made by leather, natural (crepe rubber) or synthetic polymers. The synthetic polymer materials used for the manufacture of this component are based on polyurethane (PUR), thermoplastic polyurethane (TPU), thermoplastic rubber (TR), styrene butadiene rubber (SBR), vinyl acetate (EVA), polyamide (PA), polyvinyl chloride (PVC), polystyrene (PS) or Acrylonitrile Butadiene Styrene (ABS) [4, 15-19]. However, PS and ABS materials are mainly used for heels. The selection of these materials will depend on their mechanical properties, price and design suitability, thereby determining the strength, quality and comfort desired for the final product, as shown in Table 2 [15-19]. Performance requirements for outsoles as footwear component, irrespective of the material, in order to assess the suitability for different end uses are established in the Technical Report ISO/TR 20880:2007 [20]. It also establishes the test methods to be used to evaluate the compliance with the requirements, including bondability.

Table 2 - General properties of different footwear materials

Materials		Properties
Natural	**CREPE (natural rubber)**	very good wear resistance very soft temperature sensitive easier to cut and trim when cold very good crack resistance limited in colour
Natural	**Leather**	fibrous and porous material flexible material (has a low Young modulus) easily damage by heat-shrinking good aesthetic appeal
Synthetic	**Leather**	
Synthetic	**PUR**	easily moulded material good cold resistance limited shelf life good durability high resistance to wear, light weight, abrasion-resistance good thermal insulation good flexibility at low temperatures excellent resistance to oils
Synthetic	**TPU**	good cold resistance elasticity low heat resistance has elasticity and durability resistant to abrasion and impact tear resistant and high temperatures
Synthetic	**TR**	moldable plastic soling excellent dry friction moldability into treated patter offers potential for high wet friction moderate abrasion resistance good performance in cold conditions very soft grades may give excessive friction cheaper rubbery aesthetic

Materials		Properties
Synthetic	**SBR**	good temperature resistance good cut resistance
	EVA	porous and flexible material excellent crack resistance
	PA	good impact, tensile, strong and flexural strengths from 0 to 150 °C excellent flow friction properties good electrical resistivity very hard
	PVC	has a wide range of rigidity or flexibility economical material easily injection moulded either directly against a leather upper or molded as all-PVC wellington boots durable material strength improves as it is made softer
	PS	rigid material ease to process
	ABS	very good balance of physical properties

2.4. Footwear manufacture process

For the manufacture of the shoe it is necessary to take into account the operating processes, divided in eight distinct steps. The steps are: storaging, modeling, cutting, sewing, lasting, assembling, finishing and packaging, as shown in the diagram describing shoe manufacture on Figure 2 [9, 21-23].

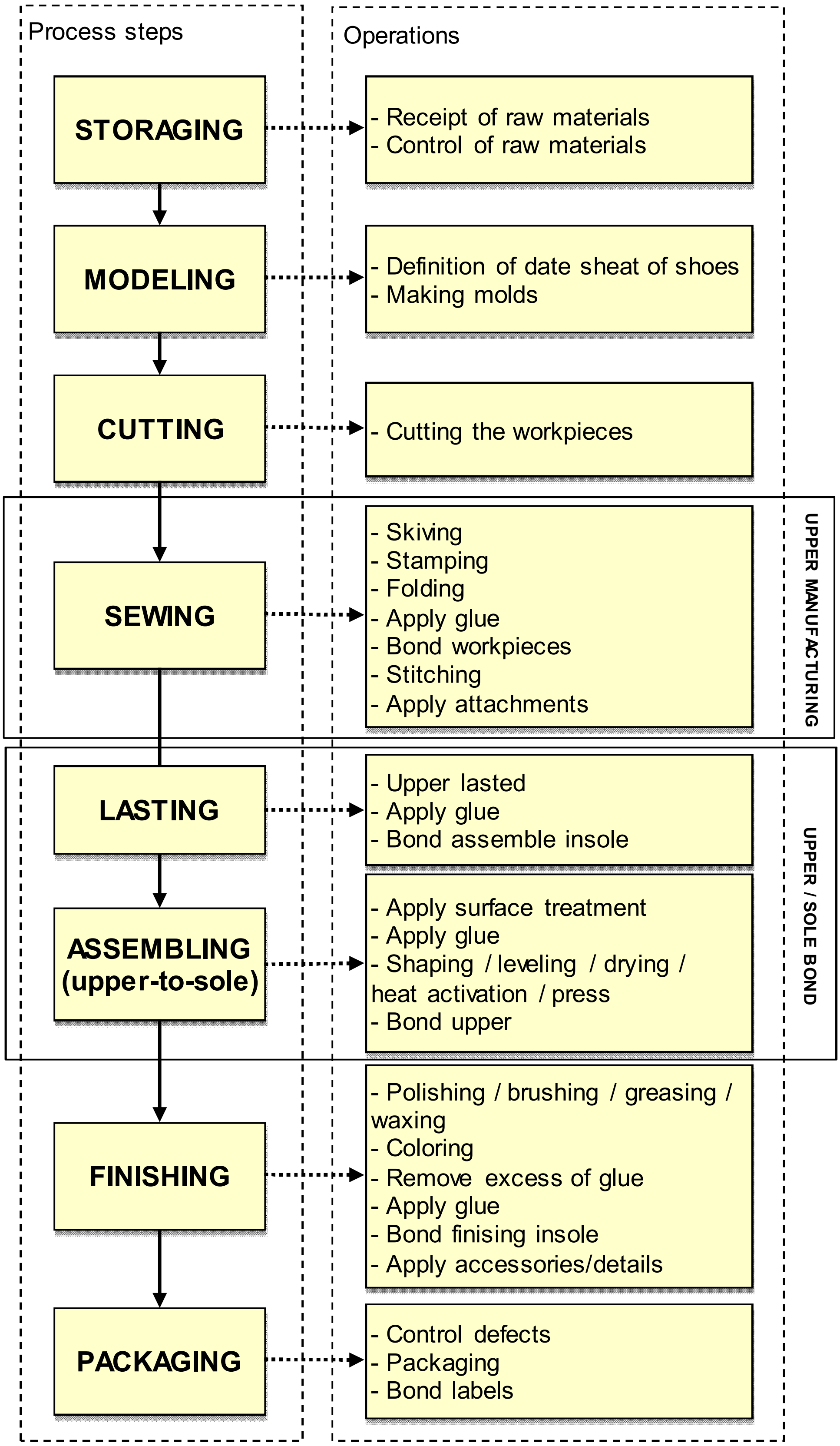


Figure 2: Diagram of a typical shoe manufacture process

Many operations involving adhesives are made generally out of the factory (i.e. heel, sole and insole preparation) and they should be also included.

In storaging, the necessary raw materials for the manufacture of footwear are identified and controlled [21]. In modeling, the shoe is created and the parts needed to build the shoe are defined. The creation of the model is determined by the fashion tendencies and the technical capabilities, setting up the shoe and attributes in its data sheet [21], defining the materials, the colors, the details, the control parameters [21-22], the molds and scale the same for all sizes that are intended to be produced [21]. In the cutting step the materials are sorted and prepared, then the pieces created by modeling in industrial quantities are obtained [1, 21, 24]. The cutting process can be manual or use automated systems to obtain all the parts of the shoes [21, 24]. When the cutting is manual, a work table and a "cutter knife" are used. The knife consists in a steel blade with a brass coating. To obtain the pieces, the hand held cutter knives or, alternatively, a cutting molds can be used [1, 9]. When the process is automated, a swing arm cutting press is used. An example is shown in Figure 3. Currently the cutting is made by using machines with a laser or waterjet cutting system integrated with the CAD/CAM software, as shown in Figure 4.

Figure 3: Swing arm cutting presses

Figure 4: Machine with laser cutting system

The cutting step is followed by the sewing procedure. In sewing the pieces are skived (which consists in reducing the leather thickness at the edge of the part, to allow for their overlap), folded (a step consisting of folding and fixing the edge of the workpiece with a latex or cement (natural rubber based glue) [4, 12, 25], underlined, crossed out, glued and sewn together, all in accordance with the instructions set by the modeler for the model to be built. The placement of accessories such as eyelets may also be required. In this phase the upper is manufactured, [9] being stitched using stitching machines, as shown in Figure 5 [24].

Figure 5: Stitching machine

The next step is the lasting, where the insole is prepared and adjusted to the upper using the last. For the manufacture of shoes it is essential to use a last, made of wood or plastic, adjusted to the shoe model and to the size. The last gives the shoe its shape [12-21]. After this step, the insole and upper are bonded to the sole [3, 9] in the upper-to-sole bonding process – assembling step. Upper-to-sole is the adhesive joint with higher technical requirements in the footwear construction.

In the assembling, soles may be attached to the upper in a variety of ways, by welted, directed moulded, pre-formed as units, cemented or stitched to it. When cemented, it's necessary to take into account the selection of the appropriate adhesive [2-4].

In the finishing step, there is a rework process, necessary to improve the aesthetic of the shoe. Here, the shoe may be subjected to brushing, greasing, polishing, waxing and even to the application of paint (coloring) [12-21]. Accessories like cords and labels are applied, excess adhesive is wiped and cleaned and the finishing insoles are bonded into place [21]. The process ends with the inspection, where the shoes are subjected to observation and comparison of the two shoes of the same pair in order to verify if they meet the specification required by both the modeler and the client.

The packaging step is where the shoe is placed in boxes and labeled with an indication of the model and the number. Here the final quality control is also made, where the shoe is last checked for defects. From this moment the shoe is ready for expedition and to be delivered to the final market [9, 21].

As shown by the descriptions presented above, during the manufacturing process of footwear various different materials, including adhesives, are involved in the sewing, lasting, assembling, finishing and packing steps [21].

3. ADHESIVES USED IN FOOTWEAR INDUSTRY

3.1 Introduction

As for the other materials used in shoe manufacturing, the selection of the adhesive to manufacture the adhesive joint is very important to ensure a good quality and durable final product [1, 3]. The correct choice of adhesive is fundamental to ensure the bonding strength required by both the shoe manufacturers themselves and the applicable standards, such as EN 1392:1998 and EN ISO 17708:2003 [2, 23]. In the footwear industry, the most important method for joining materials is the use of adhesives. The purpose of these adhesives is both to fill gaps and act as a connecting bridge between the materials intended to be bonded [26-27]. There is not, however, a perfect adhesive that can be used in all situations. The selection of the adhesives and the joint geometry is relatively complex and depends on various factors such as the intended final joint strength and intended shoe use, the nature of the substrates, thermal resistance and the time available to complete the bonding step, price, etc. The use of adhesives in the footwear industry is a constantly evolving process, always guided by advances in chemical knowledge and methods.

Nitrocellulose adhesives were among the first to be introduced, as far back as 1906. The adhesives were mostly replaced in 1949 by polychloroprene (PCP) adhesives due to their versatility, as they present good results in bonding leather, textiles and other materials, such as vulcanised rubbers. The introduction of plastic materials to the footwear industry containing high amounts of plasticisers made necessary the search of alternative adhesive, with these anti adherend plastic substances. For that reason, in 1970 adhesives based on thermoplastic polyurethane were introduced, which are the most common adhesive used currently for upper-to-sole joints due to their high versatility. PCP and PU adhesives are mainly used for high demanding strength resistance joints such as upper-to-sole. Furthermore, other adhesives based on synthetic and natural polymers such as styrene-isoprene-styrene (SIS), styrene-butadiene-styrene (SBS), styrene-butadiene rubber (SBR) latex, hotmelt (polyamide, EVA based), etc, are used in the different footwear operations previously described [2, 4, 28].

The market constantly poses new challenges for the adhesive manufacturers, guided by fashion trends, innovative designs, increasing performance requirements and environmental concerns, such as legal constraints imposed by Regulation (EC) n. 1907/2006 of 18 December 2006, also known as REACH (Registration, Evaluation, Authorization and Restriction of Chemicals). Lately there is a strong requirement for the replacement of solvent borne adhesives in order to improve workers health and avoid environmental concerns. Furthermore, for shoes with European Ecolabel the use of organic solvents are limited. However, solvent based systems still continue to be used because of their performance [27]. Currently, there is a drive for the development of water based adhesives, strong enough to satisfy the needs of the market. However they do require adjustments in the shoemaking process of the manufacturers, mainly due to the drying time and slight different application. For this reason and also because of the low price of the solvent borne adhesives, the footwear industry still mainly uses solvent based adhesives [4].

In different steps of the footwear manufacture have distinct requirements in the adhesives. For example, during the lasting step, it is necessary to use a PCP or a hotmelt adhesive such as polyester and polyamide type [25]. The hotmelt used on footwear manufacturing is a thermoplastic polymer that is applied on the substrate at a temperature above it’s the softening point, reaching high cohesive strength upon cooling [25]. For bonding the lining to upper material, adhesives based on NR (natural rubber), SIS, PCP solvent based or latex could all be used [29-33] generally with low bonding strength and tack. The choice can depend on such factors as the kind of application (brush or spray) and if the bond is followed or not by the stitching, as shown in Table 3.

Table 3: Different kinds of adhesives used on sewing

Adhesives solvent base	Spray		Brush	
	With stitching	Without stitching	With stitching	Without stitching
NR				X
PCP			X	
SIS	X			
Latex		X		

The following section describes in more detail the most commonly used adhesives in the footwear industry.

3.2 Types of adhesives

3.2.1 Hotmelt

Hotmelts are thermoplastic adhesives, 100% solid content and solid at room temperature but become fluid at higher temperatures. Main components of hotmelts: polymer, wax's, resin, etc. The application of heat melts the adhesive, allowing the connection of the surfaces to be joined and producing a high degree of wetting between the adhesive and the adherend. After application, the temperature is reduced and the adhesive solidifies, developing maximum strength. The use of hotmelt allows the quick production of an adhesive joint, reducing time in the assembling step. In footwear usage, these adhesives are characterized by their flexibility and resistance to moisture and body oils without difficulty, which permit the easy fabrication of complex shapes [25, 32], depending on the adhesive composition.

3.2.2 Waterborne adhesives

Waterborne adhesives are dispersions or emulsions composed of polymers in water. The main advantage of using this type of adhesives is the elimination of toxicity or flammability problems. These types of adhesives are non-toxic and non-inflammable. Furthermore you can obtain adequate bond strengths achieving good performance adhesives. In some cases the drying of these adhesives may be slower, requiring the need of forced drying systems [34].

These adhesives have higher price due to a higher solid content than solvent based ones. Therefore, the amount of adhesive applied should be lower. As a result, suitable and similar drying times are obtained, which results in optimum yield and efficiency [34].

3.2.2.1 Latex Adhesives

The rubbers most commonly used for latex adhesives used for shoes manufacture are natural rubber (cis-polyisoprene) and PCP types [4]. Latex is an aqueous dispersion presenting approximately 60% solids, which corresponds to the percentage of rubber in the solution. It is characterized by easy handling due to its viscosity, it has a high solids content, it does not contain solvents [28, 35], and is thermo-oxidative stable [4].

These adhesives are usually applied for bonding porous substrates such as leather, paper and textiles [28-29, 35]. Latex adhesives are used as water based contact adhesives, presenting an instant bond with sufficient green strength [29-30].

3.2.2.2 Polyurethane Adhesives (PU)

PU waterborne solutions are applied as adhesives and coatings in textiles, metals, plastics and woods. These adhesives are widely used for upper-soles joints, presenting flexibility, good behavior at low temperature and high strength. Waterborne PU adhesives are a good alternative to PU solvent based adhesives, however, they require additional heat in the process to remove water before joining is completed [34].

3.2.3 Solvent based adhesives

Solvent based adhesives are composed of a polymer dissolved in an organic solvent or mixture of solvents. They are currently the most common used adhesives in the footwear industry and hence are the ones subject to more attention in this work.

3.2.3.1 Polyurethane Adhesives (PU)

Solvent based PU adhesives are characterized by their flexibility and performance at low temperatures, the excellent adhesion and cohesion strength, and also for rapid curing. These adhesives have good wettability in a wide variety of materials. They form covalent bonds with substrates that have active hydrogen atoms on the surface [35, 40-41]. The mechanism is outlined in Figure 6 [35].

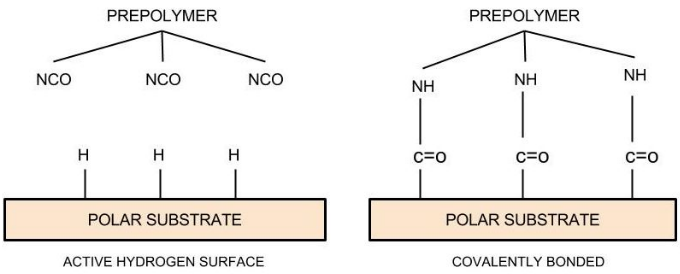


Figure 6: Mechanism of typical covalent bond between the PU adhesive and a polar substrate

In both systems of PU and PCP adhesives, we can find monocomponent and bicomponent adhesives types.

Monocomponent adhesives (1K), as the name suggests, are composed of only one component (adhesive only), and depend only on themselves to form the adhesive joint [42]. The process of physically fixing occurs after the adhesive joint is subjected to pressure [4, 36, 42].

Bicomponent adhesives (2K) are composed of two components, usually called A and B [42]. Component A is an adhesive and component B is the crosslinking compound, commonly isocyanate based. These adhesives are used when it is desired to accelerate the curing of the adhesive and increase the temperature resistance of the adhesive joint as well as durability. Therefore 2K adhesives are supplied separately, because when they are mixed the lifetime of the combination is much reduced. It is necessary to be efficient when mixing the two components to ensure a complete reaction. Only with a complete mixture of the two components the full mechanical properties of the adhesive can be assured [3-4, 36-37, 42].

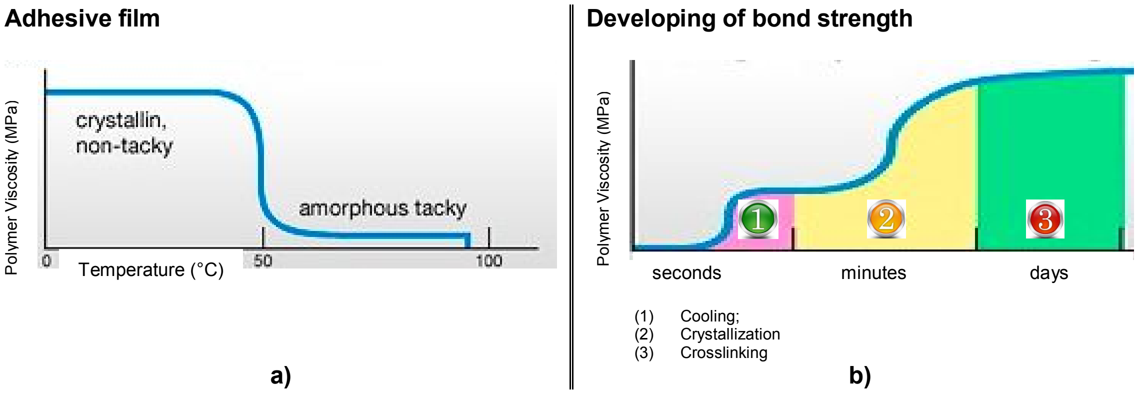


Figure 7: Curing procedure of an adhesive with 2 compound (2K) PU-based solvent: a) Tack development in adhesive film, during heat activation; b) Development along time of the bond strength in a single lap joint

In the particular case of the PU adhesive film, once it is applied and dried, it does not present any kind of tackiness. Only when subjected to temperature, the film of adhesive softens and acquires the necessary tack for attaching the substrates [4, 36], as shown in Figure 7 a). PU is a contact adhesive. Heat activation is necessary in order to acquire tack to allow the intime joint of both adhesive layers.

Figure 7 b) shows that the evolution of the curing time for a 2 compound PU solvent based adhesive. After the adhesive is applied, dried, reactivated with temperature (where the adhesive softens) and bonded by pressing the materials, the adhesive joint cools and the adhesive film dry in seconds. After a few minutes, the crystallization of the PU occurs and the curing process is almost complete. The action of isocyanate (second compound, 2K) occurs after a few days, corresponding to the complete cure of the adhesive. At this time, the curing process is irreversible, which means that the adhesive is permanently crosslinked. After crosslinking, the adhesive joint is heat resistant, so if the adhesive film is subjected to high temperatures, degradation may occur [4, 42].

3.2.3.2 Polychloroprene Adhesives (PCP)

The bonding strengths obtained using PCP adhesive solvent based are similar to those obtained using PU adhesive. The main difference between these two products is the open time, which is longer in the case of PCP. In addition, the dry adhesive film of PCP has tackiness at room temperature, allowing the fixation of the material without resorting to temperature. The length of this phase with tackiness can range from a few minutes to hours, depending on the type of resin used in the formulation [38-39, 43-44].

The solvent based PCP adhesive, known as contact adhesive, refers to an adhesive that is applied to both substrates to be bonded and allowed to dry before pressing the two substrates together to complete the bond. This type of adhesive requires high initial bond strength and the ability to form bonds with minimum pressure after long open assembly periods [19, 38].

3.2.3.3 Styrene-Isoprene-Styrene Adhesives (SIS)

Solvent based SIS adhesive has with high solid content [4]. These adhesives exhibit a good combination of high elasticity, low hardness, good balance of tack and low viscosity. They adhere to a variety of substrates, plastics, foam, and have high mechanical performance.

This type of adhesives are not used in footwear industry, in upper-to-sole joints, because of they lack the abrasion resistance under rapid loading that is required for high performance shoes [32].

3.2.3.4 Natural Rubber Adhesives (NR)

Commonly named as cement in the footwear industry, NR do not have a polar group attached to the polymer and for that reason they do not bond to polar surfaces. These rubbers have poor thermo-oxidative stability. These adhesives are used in applications where the requirement is for temporary bonding [4], for example, before sewing.

Solution adhesives consist of solid rubber dissolved in aromatic hydrocarbon solvents, depending on the drying time required [4, 28]. The adhesive is dried at room temperature or in hot air ovens [28]. Their main property is a quite long open time (sometimes more than 24 hours).

3.3 Composition of solvent based adhesives

Adhesives for the footwear industry are comprised of a variety of chemical compounds, tailored to allow the union of specific types of substrates. The components of these adhesives must be carefully selected to improve the overall performance when bonding certain types of materials [27, 37]. The main components of adhesives are elastomers, resins, additives and solvents [39].

The following sections describe each one of these components and their importance on the adhesives properties.

Elastomers

Generally, elastomers improve the elasticity and the viscosity on the adhesive and serve also as a carrier for the resins and additives [36, 38, 41]. Various types of elastomers can be used such as PUR, PCP, SIS and NR [4, 38].

The **PUR** used in solvent based adhesives is of thermoplastic nature and it has linear chains and are composed primarily of crystalline segments. It has a low glass transition temperature (Tg) and despite the high degree of crystallization present gives good flexural properties at low temperatures [4, 26, 45-46].

The different types of PU existing in the market for application on adhesives differ in the degree of crystallization (due to a relationship between the hard and soft structures) and molecular weight (which determines the viscosity). Higher molecular weight means higher functionality of the polymer, which reflects into better cohesive properties [36]. Very high molecular weight PU has quite high viscosity, low wettability into porous materials such as leather and so high temperature activation.

The balance between the crystalline and amorphous segments of the PU allows softening at low temperatures, favoring the joining process. Increased thermoplasticity and tackiness of the adhesive are useful to ensure good bonding of materials. Therefore different types of PU are mainly characterized by their degree of crystallization and thermoplasticity, which changes according to the type of monomers used and its ratio. The degree of crystallization measures the rate at which the PU, when cold, passes from the melt state to the crystalline state, as shown Figure 8 a). Therefore the crystallinity will affect the rate of development of the connection as well as the initial bond strength and tack time [36, 42], as shown in Figure 8 b).

Table 4 shows the main differences between high and low crystallization in PU [36, 47].

Table 4: Differences between high and low degree of crystallization of polyurethanes [28, 37]

Degree of crystallization	Properties
High	High temperature resistance High the peel strength Low open time High cohesion High wettability
Low	Low temperature resistance Low peel strength High the open time

A typical composition of a PU solvent based adhesive for upper-sole attachment is given in Table 5.

Table 5: Typical composition for PU solvent based adhesive, phr (parts per hundred parts of rubber)

Raw-materials	Quantity (phr)
PU	100
Resin	0-5
Fumaric Acid	0-3
Silica /Nitrocellulose	0-10
Solvent mixture	500

PCP is a versatile material because the elastomer has a combination of properties that make it suitable for many applications [39]. The most important characteristics of PCP are high mechanical strength, good chemical resistance, good acid resistance, very good adhesion to metals and textiles [4]. The adhesives made with PCP are easily crystallizable [39]. The main properties of these adhesive are adhesion to a wide variety of substrates, good initial bond strength, good cohesion, and good resistance to aging and chemical degradation agents [39, 48].

PCP adheres to a variety of substrates due to the presence of a chlorine atom in each monomer of the polymer, which gives it a very strong polarity and enables the development of physical interactions [4]. This characteristic is the reason behind PCP’s immediate capacity to bond to itself when subjected to a small pressure. This happens regardless of its level of crystallization

[47]. A typical composition of a PCP solvent based adhesive for upper-sole attachment is given in Table 6.

Table 6: Typical composition for PCP solvent based adhesive, phr (parts per hundred parts of rubber)

Raw-materials	Quantity (phr)
PCP	100
Resin	30
MgO	4
ZnO	5
Water	1
Antioxidant	2
Solvent mixture	500

SIS is a thermoplastic elastomer, belonging to a class of materials that combine elasticity of the elastomer and thermal reversibility. This elastomer can be used in applications where there is the need for flexibility and elasticity at moderate temperature and deformation conditions [38]. The SIS type polymers allow the production of adhesives with strong and lasting tack properties [43]. Its means long open time. A typical composition of a SIS solvent based adhesive is given in Table 7.

Table7: Typical composition for SIS solvent based adhesive, phr (parts per hundred parts of rubber)

Raw-materials	Quantity (phr)
SIS	100
Resin	100
Antioxidant	2
Solvent mixture	300

NR is quite sticky and it doesn't need any resin. Adhesives using NR, have higher strengths and lower elongations than those using SIS rubber [35]. NR are prone to oxidative degradation due to their main chain double bond. It's necessary to add resins to the NR adhesives formulation to achieve high peel adhesion [26]. The gel content breaks down with the mastication of the rubber, which causes the breakdown of the polymer chains and lowers their molecular mass, representing a decrease of the viscosity, easing the manufacturing and the application process [43]. The crystallization of the NR causes self-reinforcement, resulting in high tensile and tear strengths [43]. A typical composition of a NR solvent based adhesive is given in Table 8.

Table 8: Typical composition for NR solvent based adhesive, phr (parts per hundred parts of rubber)

Raw-materials	Quantity (phr)
NR	100
Resin	100
Antioxidant	2
Solvent mixture	700

Resins

Resins are used in adhesives when there is a need to influence the tackiness, the cohesion strength, open time and temperature resistance [49]. The resins allow increasing tackiness and the wettability, facilitating the bonding formation and, therefore, improving the strength by increasing the cohesive strength of the adhesive [4, 36, 49]. The improvement in properties that they generate enables the adhesives to form a reasonable bond strength immediately on contact with another substrate, with or without the application of pressure [49]. The most commonly used type of resins in adhesives solvent based are colophony, hydrocarbon, alkyl phenolic, terpene phenolic, coumarone-indene resin's.

Colophony, also known as rosin resin, increases tackiness but decreases the cohesion strength [42, 50]. These resins are, however, very sensitive to oxidation. Hydrocarbon resins are thermoplastic, which improves the initial bond strength [36, 50, 71]. The improvements brought by the resin to the adhesive are varied depending on the resin type used. There are resins that increase the open time of the adhesive, increase resistance to fatigue, act as process aids, increase the flexibility and improve the incorporation of fillers. Alkyl phenolics enhance adhesion and give an increase in the cohesive strength [38]. Terpene phenolics tackiness increases with the increase of temperature. Furthermore, terpene phenolics resin promote the reduction of the crystallization degree of the adhesive [42]. Coumarone-indene resins tackiness increases with the increase of the temperature as the terpene phenolic resins, promote the reduction of the crystallization degree of the adhesive and increase the cohesive strength and elasticity of the adhesive [38]. Vinyl chloride / vinyl acetate promotes adhesion of PVC and metal to leather, paper, wood or plastics. It also gives flexibility or hardness, depending on vinyl acetate content, and chemical resistance. Vinyl chloride is responsible for increases in adhesive strength and resistance to water and chemicals. Vinyl acetate increases the solubility and is responsible for increases in the flexibility. The resins are soluble in the common solvent used in the adhesives and are compatible with almost any other polymers and resins, depending on the concentration.

In Table 9 a summary of the general properties of resins can be seen. It shows the relative influence of each type of resin in the general properties of the adhesive [19, 35].

Table 9 - General properties of resins

Resin Types	Acidity Index	Strength	Tackiness	Open time	Temperature resistance	Elasticity	Life time
Colophony	155 – 175	↓	↑	↑	↓	↓	Long
Hydrocarbon	< 0,1	↓	↓	↑	↑	↓	Long
Alkyl phenolics	--	↑	↓	↓	↑	↓	Short
Terpene phenolics	60 – 70	↓	↑	↑	↓	médium	Short
Coumarone-indene	< 0,5	↑	↑	--	↓	↑	Short
Vinyl chloride / vinyl acetate	--	↑	↓	↓	↑	↑	Long

Additives

Additives give specific characteristics, such as preventing oxidation, higher adhesion, increase of the viscosity and solids content among others [35-36]. A large variety of additives can be found in the formulation of adhesives for the footwear industry. Fumed silica, nitrocellulose, acids, chlorinated rubber, zinc oxide, magnesium oxide, antioxidants are some of the most common [35, 39].

Fumed silica is added to promote bonding to porous substrates (for example leather, textile), because it avoids the excessive penetration of the adhesive in the substrate. It is also used to adjust the viscosity and rheology (thixotropic, pseudoplastic) [35, 39]. It also influences the mechanical properties, particularly it increases the resistance to initial peel and increases the cohesion strength due to the presence of hydrogen bridge bonds that are formed between the silane and urethane groups, favored by the presence of silica. Nitrocellulose can increase the viscosity of the adhesives. Acids act as adhesion promoters to soles of SBR. The most commonly used acids are fumaric acid and malonic acid [35]. Chlorinated rubber increases adhesion to rubber materials and increases resistance to temperature [35].

Zinc oxide (ZnO) is an activator in NR and SBR, and acts as a curing agent for vulcanization of the PCP [38-39]. It usually represents a very small proportion on adhesive, around 5% of the weight of the rubber [35].

The magnesium oxide (MgO) is used in the composition of adhesives containing chlorine atoms and acts as a chlorine acceptor in order to prevent the formation of hydrochloric acid. This prevents oxidation and aging of the adhesive, and thus prevents degradation of the adhesive properties [35, 39].

Antioxidants are used to prevent or retard the aging of the adhesives. Such aging manifests itself in variations of the hardness, color changes or degradation of the physical properties. In extreme cases it can cause the appearance of cracks immediately after application of the adhesive on the substrate [35, 38-39]. Aging occurs because of successive oxidation reactions in the polymer chain. Thus, the oxygen absorbed over time may be responsible for the degradation of macromolecules expressed by softening in the presence of heat or cold hardening and fragility [39]. When polymer degradation occurs due to attack by the oxygen produced by mixing the rubber with the resins, there is a decrease in adhesion force. Such attacks can be reduced with the addition of an antioxidant [39]. Thus, when an adhesive shows a loss of tack, attack by oxygen or environmental moisture can be suspected as causes. The compounds used in order to act as antioxidants are secondary amines, diamines and their derivatives, quinoline compounds, dithiocarbamates, alkyl-phenols, esters of phosphoric acid, phenolic [39]. Thus, we can say that antioxidants will inhibit or make a negative catalysis of auto-oxidation [38].

Solvents

The liquid portion of the adhesives is composed of organic solvents. Their main role is acting as carrier allowing adhesive application. The solvents are mainly responsible for the level of toxicity of the adhesive for the control of the drying time and provide better or worse wettability of the substrate. They also define the level of viscosity, influencing the fluidity, which can be an important parameter to be considered (depending on application method) [1, 52-53]. Various types of solvents suitable to produce adhesives solvent based are available in the market. Among these the most used are aliphatic hydrocarbons (cyclohexane, toluene), chlorinated hydrocarbons (dichloromethane), ketones (acetone, MEK), esters (ethyl acetate, methyl acetate) and tetrahydrofuran (THF) [1, 38].

However, chlorinated hydrocarbons, due to their toxicity and taking into account the legal requirements, have a tendency to disappear in the composition of adhesives [1, 36, 38]. Also to be taken into account are the legal constraints imposed by Regulation (EC) n. 1907/2006 of 18 December 2006, also known as REACH [38].

4 MANUFACTURE OF JOINTS IN FOOTWEAR INDUSTRY

For the manufacture of an adhesive joint, the type of materials that will be joined and the model of the shoe should take into account. These factors are crucial for the selection of an appropriate adhesive for the manufacture of a suitable resistant adhesive joint [2] [3].

Depending on the type of substrates, it can be necessary or not to apply a surface treatment before proceeding to the application of the adhesive, as described in section 4.2.

In the footwear industry, depending on the model of the shoe, there are three methods of fixing materials:

- Fixing by glue,
- Fixing by stitching,
- Fixing by glue and stitching [2].

In the different upper preparation steps, the assembly of the different components can be performed by using adhesives and / or stitching. In this step, various types of adhesives can be used and then selection depends on the type of materials and the adhesive joint requirements [14]. Table 10 shows the adhesives more commonly used for each operation of the sewing step [2, 19, 27].

Table 10: Adhesives applied in the sewing step

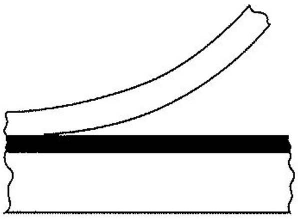
Units operations	Types of Adhesives	Bond strength
lining leather/ leather	NR adhesive solvent based, latex	moderate
leather / leather	PCP adhesive solvent based, SIS adhesive solvent based	high
leather / woven	NR adhesive solvent based, Latex	moderate
leather / foam	NR adhesive solvent based, Latex	moderate
leather (folding)	Hotmelt	high

In lasting step, depending on the procedures used for manufacturing footwear, the insole can be bonded or stitched to the upper. If it is bonded, a specific machine for the application of the adhesive (hotmelt in this step) is used, as shown in Figure 8. Different types of hotmelt adhesives are used depending on forepart lasting, waist lasting or backlasting. Furthermore, PCP with high thermal resistance are used for lasting.

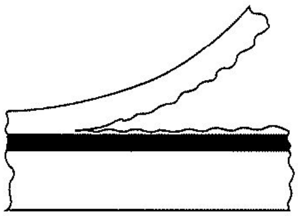
Figure 8: Machine to bond insole to the upper

4.1 Surface Treatments

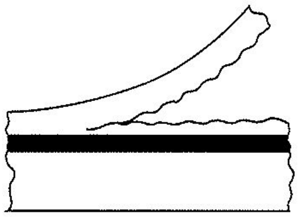
Poor bonding of materials in footwear can lead to complaints, order returns and a loss of reputation. To ensure a correct level of bond strength, surface treatment is often necessary and it can be a vital step to guarantee the durability and the quality of the bonded assembly. To generate a good bond, the adhesive must adhere strongly to the surfaces. The surface treatment must be carefully selected according to the material. For this reason it is important to analyze the type of failure that occurs in the joint when where is premature failure of a joint. There are different types of failure bond [55], as shown in Figure 9.



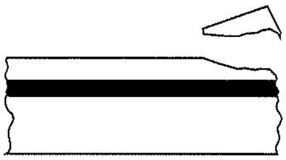
A-Adhesion failure to either adherend



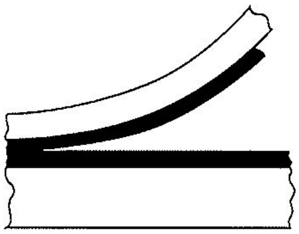
B-Surface failure of either adherend



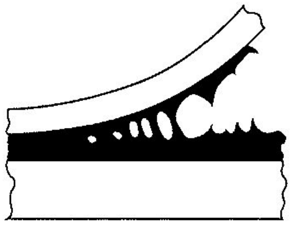
C-Deep failure of either adherend



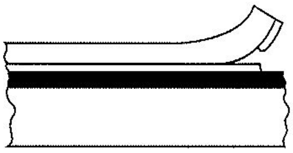
D-Tearing through either adherend



E-No-coalescence of adhesive film



F-Cohesive failure



G-Coating tear (peak force) then separation between coating and adherend

Figure 9: Different types of failure [55]

The surface treatment method has substantial effect on final adhesion characteristics [27]. For the application of the surface treatment, it is necessary to take into account the materials which are intended to be bonded [51, 55-60]. Four major types of surface treatments are available to use on the substrates: physical, chemical, primer and solvent wipping [60]. Physical treatment such as roughening using sandpaper or abrasives, increase the surface area. Chemical treatment changes the polarity of the surface. Use of primer allows minimizing the flow of the adhesive into the porous of the material to prevent the formation of weak points [54, 61] or improve the compatibility adhesive substrate. The use of solvents eliminates the release agents on the surface of the materials that might cause adhesion problems. [27, 55-59, 62]. Paiva et al [54] concluded that to maximize peel strength of the single lap joints leather/TR and leather/PUR joints, it is necessary to apply some surface treatments: on TR - chemical treatment, on leather - mechanical treatment and primer and on PU - mechanical treatment and primer. Navarro-Bañón et al [63] concluded that chemical treatment as surface treatment increases the SBS rubber surface energy and introduced surface roughness, improving the adhesion with PU and PCP adhesive types in upper-to-sole joints. Each material requires the application of a specific surface treatment, as shown in Table 11 [19, 59, 61, 64-71].

Table 11: Surface treatment vs materials

MATERIALS	CHEMICAL TREATMENT	MECHANICAL TREATMENT	PRIMER	SOLVENT WIPPING
Leather		X	X	
PU		X	X	
TPU	X			X
TR	X			X*
SBR	X	X		
EVA		X	X	
PA			X	
PVC				X
PS				
ABS			X	X

*** When a specific PCP adhesive or TR is used**

For example, **Leather** commonly has a layer of grease at the surface, which causes problems in the manufacture of the adhesive joint, thus the need to perform an adequate surface treatment [62]. The recommended surface treatment is to subject the leather to a mechanical treatment (roughening), using a P24 aluminium oxide abrasive cloth, to remove the presence of any greasy or fatty materials, like polyethylene that creates adhesion problems on the surface [58]. A primer is used to minimize adhesive penetration in to the pieces of the leather. Sometimes a specific primer can be used to make more compatible the PU adhesive with the greasy leather. After application allowed to dry for 5 to 20 minutes at room temperature [36, 62].

TR as a low surface energy material requires the application of a surface treatment to achieve an acceptable bond. The TR substrate must be subjected to a chemical treatment (halogenation) allowing reacting it to dry at least 1 hour at room temperature to improve material surface energy [55, 62, 66-71].

4.2 Upper-to-sole bonding process

As mentioned in previous sections of this work, to bond the upper to the sole in the footwear industry two types of adhesives are mainly used: PCP adhesive solvent based, PU adhesive solvent based [2, 4]. Figure 10, shows the main steps of the upper-to-sole bonding process when a PU adhesive is applied.

A - Adhesive application B - Adhesive drying C - Adhesive heat activation

D - Attach the upper to sole E - Pressing upper-to-sole

Figure 10: Application of PU adhesive solvent based on assembly step

Consequently, some fundamental shoemaking parameters must be taken into account and controlled to ensure the correct joint of the substrates. These parameters include the activation temperature, working time and contact pressure. In addition, a correct adhesive application and a proper amount applied. As shown in Figure 10, to bond uppers to soles, the footwear industry takes the following steps [4, 19, 54]:

a) Application of adhesive on the upper (Figure 10 A);

b) Application of adhesive on the sole;

c) Allow the adhesive to dry, by solvents evaporation, about 5 to 10 minutes for PU adhesive solvent based and 15 to 20 minutes for PCP adhesive solvent based at room temperature (Figure 10 B);

d) For PU adhesive solvent based, activate the adhesive by heat (infrared radiation, IR), approximately between 55 and 80 °C for 2 to 6 seconds (Figure 10 C) is required. In addition, PCP adhesive are also heat active when drying time is over open time. Activation time depends on material colour;

e) Attach the uppers and soles, placing the desired position (Figure 10 D);

f) Pressing for 4 to 5 seconds at a pressure of approximately 2 to 4 bar (Figure 10 E). The press depends on material nature and hardness. Press time depends on crystallization rate.

5 JOINT PROPERTIES

There are several factors that influence the strength of a bonded joint and to understand them it is important to precisely measure the performance of the joints. In this section there is a discussion of the mechanical properties that are more relevant for the selection of an adhesive in the footwear industry [62]. There are two mechanical properties considered important in the manufacture of footwear, peel strength and creep strength. Each property requires a specific test for its evaluation [4].

The upper-to-sole requirements are defined on EN 15307 [6], as shown in Table 1.

5.1 Peel strength

The peel strength is the property that determines the necessary force to separate two materials, in joints where at least one of the substrates is flexible. This property is determined by a peel test, allowing to distinguish if an adhesive is brittle or ductile. This test is performed in a tensile testing machine [6, 55, 62, 72-73]. The peel test is a standardized method and for the footwear industry standard EN 1392 is used as a reference standard [55]. This standard determines the test method for obtaining the peel strength at an angle of 180°, with the materials bonded in the specimen shape shown in Figure 11 [55].

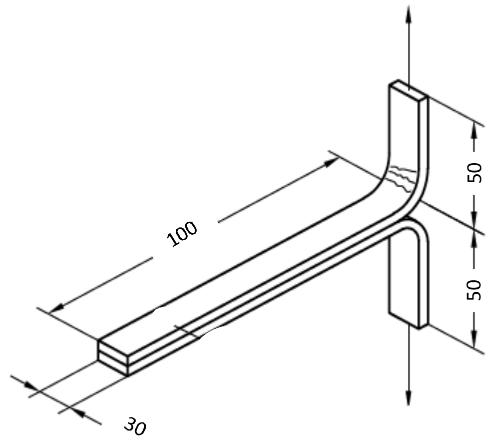


Figure 11: Adhesive joint for peel test (dimensions in millimetres)

72 hours after the manufacture of the adhesive joint, the peel test is performed in a testing machine at a speed of 100 mm/min [6]. The peel strength per unit of width is determined by the ratio between the average force (Newton, N) and the average width (millimetre, mm) of the overlap joint [55, 73] defined as:

$$P = \frac{F}{A} \tag{1}$$

where P is the peel strength (N/mm), F is the average force (N) and A represents the bonded joint width of the specimen (mm) [73]. The values of F and A are obtained from the force/deformation plot obtained experimentally.

Paiva et al [54, 62] concluded that applying solvent based PU adhesive to bond PU soles to leather upper, the peel strength is capable to satisfy the minimum requirements for the footwear industry, since applied the correct surface treatment. *Navarro-Bañóno et al* [63] concluded that is possible to obtain good results of peel strength using PU and PCP adhesive types to manufacture SBS/adhesive/leather joints, however, to eliminate the reactivation process with PCP adhesive it is necessary to use thermoreactive phenolic resin on the formulation.

Furthermore, the type of failure can provide useful information about the performance of the adhesive joint or in case of improvement which parameter should be improved (material cohesion, heat activation, pressure, surface treatment, adhesive viscosity, etc.)

5.2 Creep strength

Creep strength is a property that allows the assessment of the temperature resistance that the adhesive is able to withstand without suffering any loss of properties and without suffering damage to its structure. This property is important for footwear because footwear can be subjected to surprisingly large temperature gradients. As an example, when the shoes are exhibited in shop window displays, they are subjected to large temperature variations. To quantify this property the creep test is performed, which is normalized according to the standard EN 1392 [55]. This property is very important also for adhesives to be used for lasting where high thermal resistance is required. A schematic of the joint used for creep test and the loading condition is shown in Figure 12.

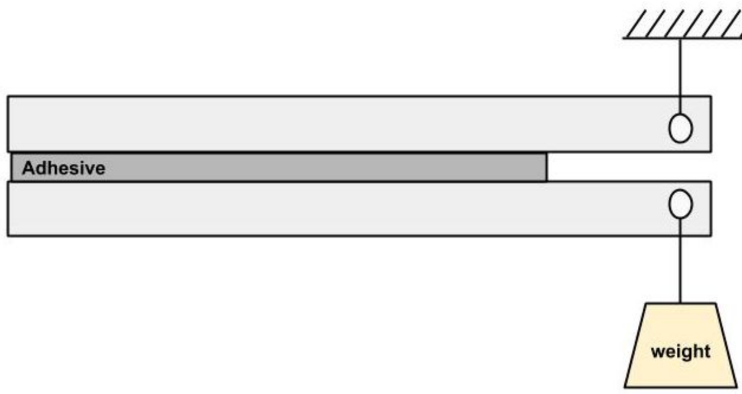


Figure 12: Adhesive joint for creep test

After the complete cure of the adhesive joint, the creep test is performed in a controlled environment at a temperature of 60 °C. This temperature is chosen to simulate the warming of footwear in, for example, non-temperature controlled shop windows, in transit in warm climates or on exposure to high temperatures in service. The test procedure is started by carefully bending apart the unbonded ends of the test specimen, marking the beginning of the bonds, and inserting the ends in the clamps of the peel test chamber. This is followed by heating the test pieces in the test chamber for 1h to allow them to reach the specified temperature. After this heating up period, each of the test specimens is loaded for 10 min with the specified constant weight (1,5 kg). The peeling strength provided by the 1,5 kg mass are sufficient for standard test. Higher peeling strength, corresponding to the 2,0 and 2,5 kg masses, may be used for special proposes, such adhesives with very high heat resistance. Finally the test chamber is opened and the deformation of specimen is measured (in millimetres, mm) while still loaded. The time (in minutes, min) to complete separation is then determined [6]. With the creep experiment a “creep rupture envelope” which can be obtained, divided into three phases: primary, secondary, and tertiary. The primary phase corresponds to instantaneous elastic strain, the secondary phase represents the creep rate and the tertiary phase occurs with the rupture of the bond of the specimen [4, 40]. The results are expressed displacement (millimetres, mm) versus time (minutes, min).

Gao et al [74] concluded that the effect of temperature on the creep loading is very evident, finding that the creep rate increases with an increase in temperature. The work of *Paiva et al* [75] has shown that, for the footwear industry, good results for creep rate are reached when materials such as PU, caprolactone with extremely high crystallization type, and some additives, like fumaric acid and chlorinated rubber, are included on the adhesive formulation. Inversely, when colophony and vinyl resin are included, there creep results are noticeably worse.

6. CONCLUSIONS

This review shows that in the footwear industry the adhesives assume a very important role to ensure the quality of the final product.

For that reason, before selection of the adhesive, it's very important to define all the materials necessary to manufacture the shoes and to define the intended type of union of materials and what the method of application. The surface treatment can then be selected in accordance with the materials to be used. Considering the most demanding joint on footwear, upper-to-sole, we can identify a few commonly used materials. For the upper, PVC, natural and synthetic leather are usually employed. For the sole, crepe, natural or synthetic leather, PU, TPU, TR, SBR, EVA, PA, PVC, PS or ABS are used.

A correct surface treatment is important to achieve the required level of performance from the adhesive joint. The effects of such treatment are varied, being able to enhance the wettability, the surface chemistry and/or to remove the surface finishes, improving the compatibility with the adhesive. In the footwear industry the most commonly used surface treatments are the primer, solvent cleaning and physical and chemical treatment (halogenation).

The adhesive composition may contain elastomers, resins, additives and solvents in order to meet the intended mechanical properties.

In the footwear industry, more specifically in the bonding upper-to-sole, two important mechanical properties are controlled. These are the peel strength and the creep strength. These properties are standardized in EN 1392, EN 17708, the technical requirements for the different classes of footwear regarding upper-to-sole bondability are included in EN 15307.

Acknowledgements

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PAPER 2

SURFACE TREATMENT

PAPER 2

IMPORTANCE OF THE SURFACE TREATMENT IN THE PEELING STRENGTH OF JOINTS FOR THE SHOES INDUSTRY

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Abstract

In order to contribute to the research and development of adhesives for the shoe industry, this paper aims to analyze the peel strength of an adhesive joint with various types of surface treatments. In the shoe industry, the adhesive properties are very important to ensure the quality of manufacture of the shoe, thus, to better understand the behaviour of the adhesive joint, it is important to analyze the peel resistance in order to adjust the manufacturing process. For the execution of this work, we considered the following materials: natural leather, thermoplastic rubber (TR), polyurethane (PU) and a polyurethane non structural adhesive solvent based. This paper analyzes the influences of the application of chemical and / or physical surface treatments on substrates in the peel strength of a T joint. It was found that certain surface treatments, depending on the substrate, are required to obtain an adhesive joint capable of satisfying the minimum required by the shoes sector.

Key-words

Peel strength; adhesive joints; footwear; polyurethane adhesive solvent based, thermoplastic rubber, polyurethane, leather.

1. INTRODUCTION

In Portugal, the footwear industry is increasingly characterized by quality, comfort and beauty of its models. Hence, there has been an increase in exports, evident over the past years. While comfort is determined by the selection of materials and the shoe design, quality is determined by the construction of the shoe, being also a reflection of the materials used and the manufacturing process of the adhesive joint **[1].** For the manufacture of the adhesive joint, one must take into account the need for an adhesive capable of promoting adhesion required of select materials.

The selection of optimum adhesive for the adhesive joint is not always an easy task because the materials differ and, in many cases, the materials selected for construction of a model shoe are subjected to surface treatments, which increases the complexity of the manufacturing process but provides a better union of the materials.

For the manufacture of footwear it is necessary to take into account the following operating procedures: modeling, cutting, uppering, assembly, finishing and packaging. For the preparation of this work the most demanding adhesive joint was considered. The joint described in this paper is part of the assembly procedure, which adjusts the upper to the form of the shoe and proceeds to glue it to the sole. The selection of these materials will vary, depending on its mechanical properties, price and intended design, thereby determining the strength, quality and comfort desired for the final product. The upper can be on natural or synthetic leather, woven or polyvinyl chloride (PVC). The soles may be of synthetic rubber, natural rubber (NR) or leather. Synthetic rubbers commonly used in the manufacture of this component for the construction of the shoe are based on polyurethane (PU), thermoplastic polyurethane (TPU), thermoplastic rubber (TR), styrene butadiene rubber (SBR), ethyl vinyl acetate (EVA) , polyamide (PA), polyvinyl chloride (PVC), polystyrene (PS) or acrylonitrile butyl styrene (ABS) **[2]**.

For the elaboration of this work, leather was selected as the material to use in upper. For the sole, thermoplastic rubber (TR) and polyurethane (PU) were selected. The TR soles are synthesized from polymer blocks, based on butadiene and styrene. This polymer is cured under the effect of sulfur which makes the healing process irreversible. However, by heating the link is weakened and elastomers may again be subjected to a change of shape. Such an occurrence is possible because the styrenic monomers are more polar and thus more soluble than butadiene and when styrene is subjected to temperature it becomes liquid. This characteristic brings advantages, as TR can be subjected to recycling processes **[3]**. Additionally, these soles are characterized as being resistant to water, very flexible and resilient. They are also a cheaper material when compared with other materials that exist on the market. TR soles are usually used for making women shoes of good quality, presenting itself as a material that has a tendency to replace the EVA and PVC.

PU soles are a combination of polyol with isocyanate, although, for production it may also be necessary to apply additives, in particular catalysts and pigments. After mixing these substances, a reaction occurs which enables synthesis of the polyurethane compound. This mixture is made and then immediately subjected to injection moulding, allowing to mould a sole in the desired shape. This type of sole is characterized by its durability, high resistance to wear, light weight, abrasion-resistance, ease to pigment, good thermal insulation, good flexibility at low temperatures and excellent resistance to oils. As a thermosetting material it does not soften when exposed to heat. All these qualities allow the manufacture of good quality shoes **[3]**. The PU soles have wide application in sports shoes, safety shoes, men's and women footwear that require a boldest design, among others.

In the footwear industry, the most important method for joining materials is adhesive bonding. In 1906 nitrocellulose adhesives were introduced, being replaced in 1949 by polychloroprene adhesives (PCP), which due to their versatility present good results in leather bonding, textiles and other materials. In 1970 the PU adhesives are then introduced in the footwear industry. Subsequently adhesives based on styrene-isoprene-styrene (SIS), styrene-butadiene-styrene (SBS) , styrene-butadiene rubber (SBR), latex, aqueous dispersions and hotmelts were used **[4]**. However, for the bonding of upper / soles, adhesives used are based on PCP and PU. This work discusses the PU solvent-based adhesives because they are able to bond various types of materials, regarding the application upper / soles **[5]**.

As for the surface treatment, the TR soles chemical treatment is applied to the substrate to provide uniformity, allowing and increasing the cohesive strength of the adhesive joint **[6]**. This treatment allows the chemically modification of the surface to be bonded. In the footwear industry, the most commonly used chemical treatment is via halogenated substances. During production, PU soles are coated with a release agent to facilitate its removal from the mould and the footwear industry uses more than one treatment, starting with mechanical carding which is followed by application of a primer. On the leather based uppers, mechanical treatment is applied followed by the application of a primer. This treatment creates mechanical roughening on the substrate surface by increasing the contact area and therefore increasing the number of possible linkages in the interface between the adhesive and the substrate. In the footwear industry, the mechanical treatment is the most widely used, with the carding performed using the sandpaper **[6]**. The primer also works as a surface pre-treatment and consists in a polymer solution in organic solvents. This composition is related with the adhesive, but with low viscosity, forming a thin layer on the substrate. The primer, when dry, provides a very strong bond with the adhesive, requiring compatibility of the primer with the adhesive **[6]**. In the footwear industry, various methods are used depending on the application operation. In the case of bonding upper / sole, the method of application by brush is used.

Applying PU adhesive on the substrate and after the drying time, it forms a film which does not have any tackiness. Only when subjected to temperature is that the film of adhesive softens, acquiring the necessary tack for attaching the substrates. Next, the adhesive joint is subjected to pressure, followed by the cooling and thereafter is given the start of the curing of the adhesive **[4]**. Therefore, we must take into account some necessary conditions for the manufacture of adhesive joint, including the reactivation temperature, working time and pressure required to promote the desired union of substrates.

The reactivation temperature and time are determined by the need to soften the adhesive film and not the sole, enabling rapid development of bond strength. When working with soles that soften at low temperatures, it is necessary the use of an adhesive to provide a low temperature required for reactivation, so it might be possible to manufacture the joint by adjusting the time required for the reactivation of the adhesive film.

In the application of polyurethane adhesives based solvent the process identified in Figure 1 is considered.

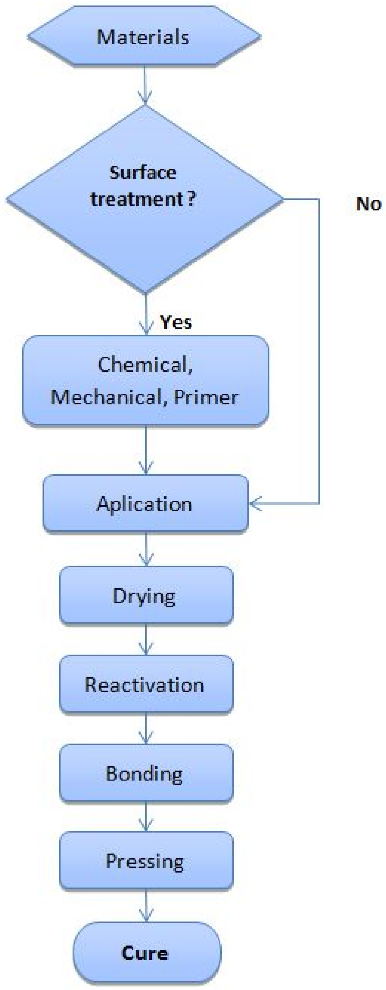


Figure 1: Process of application of the PU adhesive solvent-based

In the bonding of the upper to soles, the shoe industry follows the next steps:

a) submit, if necessary, treatment of the substrate surface;

b) apply the adhesive on the upper;

c) apply the adhesive on the sole;

d) let the adhesive dry by evaporation about 5 to 10 minutes at room temperature;

e) activate the adhesive using infrared radiation (IR) from 60 to 80 ° C for 2 to 6 seconds;

f) join the upper and sole, placing in the desired position;

g) pressing for 4 to 5 seconds at a pressure of approximately 2 to 4 bar. **[7]**

The mechanical properties considered important in the manufacture of shoes are the following: peel strength and heat resistance, properties that determine the final strength of the bond. In terms of properties, this paper focuses on the peel strength, which is intended to evaluate the mechanical behaviour of the PU adhesive solvent-based when bonding leather to TR or PU soles, while taking into account the presence or absence of surface treatments on the substrates. The peel strength is a property which determines the strength required to peel off two materials, where at least one of the substrates is flexible; it is possible to distinguish if an adhesive is fragile or ductile.

To quantify this property the peel test was performed in a tensile testing machine, which is a standard test. Two standards are used for footwear industry adhesives:

- ISO 20344:2004 (shoe),

- EN ISO 11339:2010 (specimen) **[4]**.

ISO 20344:2004 is designed to evaluate the bonding properties of soles where adhesion is measured by determining whether or not it is acceptable for the desired effect. This standard allows to obtain the peel strength per unit width, which is medium strength per unit width, applied by an angle between 90 ° and 180 °, depending on the flexibility of the substrate, in relation to joint, needed to lead to rupture. In the footwear industry independently of the type of materials used, to ensure its durability, it is necessary for adhesive joints fulfilling certain specifications defined by EN 20344 (5.2), which establishes the minimum values to consider for difficult bonding. Table 1 refers to the values required for joining upper/sole.

Table 1: Reference values of adhesion upper / soles, according to standard EN 20344

Shoes	Peel Strength per unit width (upper/sole)
baby	≥ 2 N/mm
child	≥ 4 N/mm
woman	≥ 3 N/mm
man	≥ 4 N/mm

EN ISO 11339:2010 determines the test method for obtaining the bond strength at an angle of 180 º, but using the materials in the form of specimen, as shown in Figure 2 **[6]**.

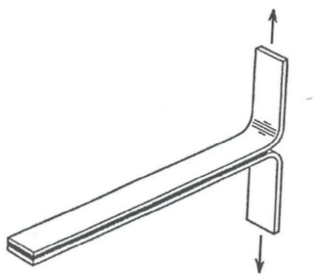


Figure 2: Adhesive joint for peel test

2. EXPERIMENTAL DETAILS

The experimental portion of this work consisted of the analysis of peel strength in the single lap joint, subjected to tensile loading.

2.1 Materials

For the elaboration of this work, TR was considered as the reference TTSC TR-2531-80C (*LINOS - Componentes para calçado, L.A.*). In Table 2 it is possible to verify the characteristics of this material, information provided by the manufacturer of the sole (technical datasheet of the material).

Table 2 - Characteristics of the TR

Characteristics	Method	units	Sonaflex TTSC-2531-80C
Density	ASTM D792	g/cm^3	0.92 – 0.98
Hardness	DIN 53505	Shore A	77 – 83
Tensile	DIN 53504	MPa	≥ 4
Elongation at rupture	DIN 53504	%	≥ 300
Abrasion resistance	DIN 53516	mm^3	≤ 250
Flexion resistance	BS 5131:2.1 (150000 cycles)	mm/Kc	< 0.1

The PU selected was Flexsol 486 (*Flexsol – Indústria de PU, Ltd.*). In Table 3 it is possible to verify the characteristics of PU used in this work, this information is provided by the manufacturer of the sole (technical datasheet of the material).

Table 3 **- Characteristics of the PU**

Characteristics	Method	units	PU 486
Density	DIN 53420	g/cm^3	0.55
Hardness	DIN 53505	Shore A	57
Tensile	DIN 53504	MPa	4.8
Elongation at rupture	DIN 53504	%	457
Abrasion resistance	DIN 53516	mm^3	298
Tear strength	DIN 53507	N/mm	8.9
Flex fatigue resistance	DIN 53543	cycles	100000

As halogenate for TR, Halinov 2190 was used (*CIPADE – Indústria e Investigação de Produtos Adesivos, S.A.*). As a primer for PU, Plastik 6109 (*CIPADE – Indústria e Investigação de Produtos Adesivos, S.A.*) was used, and as a primer for the leather the Plastik 6271 was selected (*CIPADE – Indústria e Investigação de Produtos Adesivos, S.A.*).

The two combinations of adherent materials under study were leather/TR and leather/PU. Plastik 6275 (*CIPADE – Indústria e Investigação de Produtos Adesivos, S.A.*), a solvent based PU was used as the adhesive, which has a sufficient viscosity for the effective wetting, and is able to penetrate into the cavities created by the mechanical treatment on the substrate. Table 4 shows the characteristics of the primers and the adhesive used. These values were supplied by the manufacturer (technical datasheet of the products).

Table 4 **- Characteristics of the** primers and adhesive

Characteristics	Units	Plastik 6275	Plastik 6271	Plastik 6109
Viscosity	cPs	3500-4000	250 – 300	100 – 200
Solids	%	15 – 19	18 – 21	6 – 10
Density	g/cm^3	0.82 – 0.88	0.85 – 0.91	0.83 – 0.89
Drying time	min.	10 – 15	5 – 20	60
Reactivation temperate	^{0}C	70	-	-

2.2 Geometry

In this work, for the manufacture of the joint, it was decided not to study the full sole and upper combination, but instead smaller peel specimens were manufactured.

The adhesive joint studied is composed of two substrates (150mm x 30mm) glued together in an area of 100mm x 30mm, as shown in Figure 3.

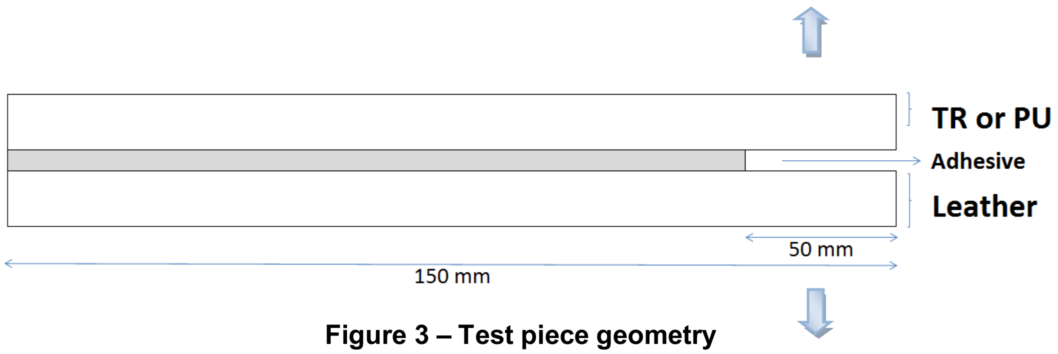


Figure 3 – Test piece geometry

2.3 Surface Treatments

For the application of surface treatment one must take into account the materials which are intended to be bonded. This work took into account the following points:

- *Variables for the surface treatment of leather*

  a. The leather substrates were subjected to a mechanical treatment;
  b. The primer (Plastik 6271) was applied and allowed to dry for 5 to 20 minutes at room temperature;

- *Variables for the surface treatment of PU*

  a. The PU substrates were subjected to a mechanical treatment;
  b. The primer (Plastik 6109) was applied and allowed to dry about 1 hour at room temperature;

- *Variables for TR surface treatment*

  a. The TR substrate was subjected to chemical treatment (2190 Halinov) and allowed to dry at least 1 hour at room temperature;

- *Procedure for the manufacture of single lap joint*

  a. The adhesive, Plastik 6275, was applied in both substrates and allowed to dry for 10 to 15 minutes at room temperature;

b. The adhesive films were activated by IR radiation at about 70 ° C for 6 seconds;

c. The substrates, leather/TR and leather/PU, were bonded in the desired position, as seen in Figure 3;

d. The adhesive joint was subjected to 2 to 4 bar of pressure for 4 to 5 seconds.

For the mechanical treatment a P24 aluminium oxide abrasive cloth was used.

The adhesive joints, after being pressed, were stored in standard conditions (23 º C, 50% Hr) during 24h, in order to ensure the complete cure of the adhesive. Only then they were subjected to the peel test.

2.3 Peel test

In the production of the adhesive joints, taking into account the material under study, the surface treatments were considered as variables, in order to be able to identify their importance in the peel strength. Therefore, the first step was making an application of all treatments commonly used in the footwear industry, followed by the manufacture of an adhesive joint without any surface treatment. In addition, joints were fabricated where only one of the treatments was performed. Other combinations were done in order to examine the effect of treatments. For the preparation of this work, for leather/TR joints, the test plan identified in Table 5 was followed.

Table 5 - Test plan for specimens leather/TR

Mat.	Surface treatment	1	2	3	4	5	6	7
TR	Chemical	■		■		■		
Leather	Mechanical	■			■	■		■
	Primer	■					■	■

In the manufacture of leather / PU joints, since the manufacture of adhesive joints leather/TR had already tested the influence of surface treatments on leather, only treatments on PU were selected as variables, as shown in the test plan of Table 6.

Table 5 - Test plan for specimens leather / PU

Mat.	Surface treatment	1	2	3	4
PU	Mechanical				
	Primer				
Leather	Mechanical				
	Primer				

72 hours after the manufacture of the adhesive joint, the peel test was performed in the testing machine at a speed of 50 mm/min. The results are expressed as load (N) versus extension (mm). The peel strength per unit of width is determined by the ratio between the maximum force and the width of the overlap joint. Three adhesive joint specimens for each test were considered. An image of the mechanical system used to obtain the peel strength is shown in Figure 4.

Figure 4 – Testing machine and mounting system

The traction machine used is an Instron, model 3367, with load cell of 30kN.

3. RESULTS

On Figure 5 are represented the load displacement curves for different surface treatments of the adhesive joints using leather/TR.

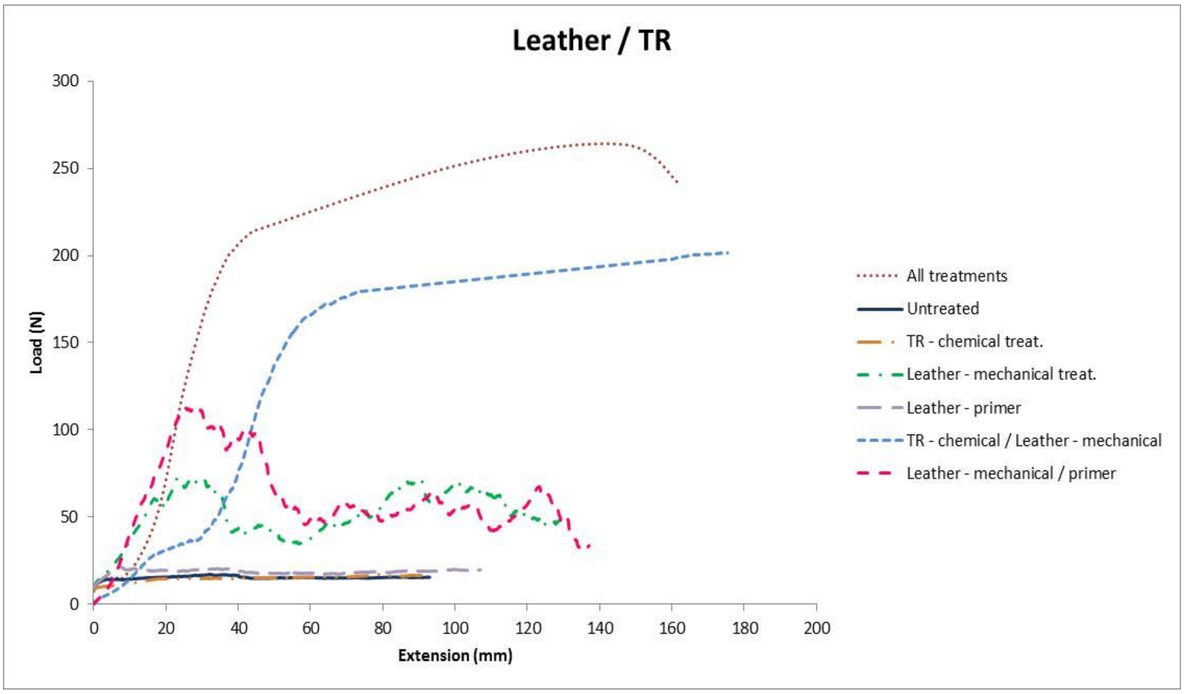


Figure 5 - Tensile tests: leather/TR (representative shown curve for each case)

Maximum strength values and standard deviation associated with each test are shown in Figure 6.

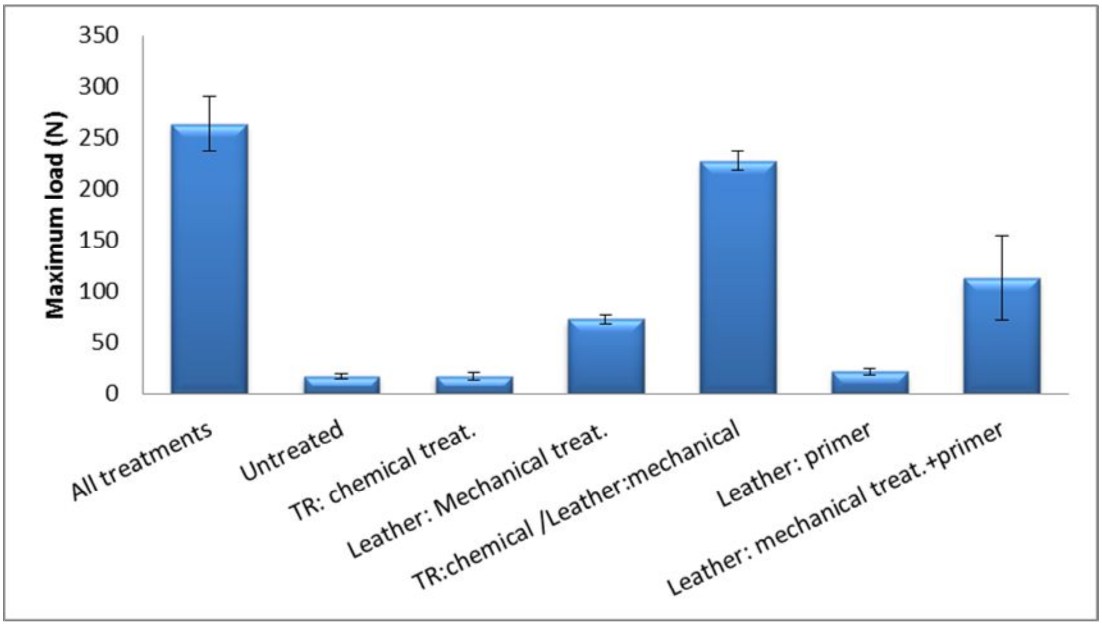


Figure 6 - Adhesive joint Leather/TR: maximum strength and standard deviation

Table 7 shows the different types of failure identified on the tested joints, divided according to their treatment.

Table 7 – Adhesive joint leather/TR: types of failure of the peel tests

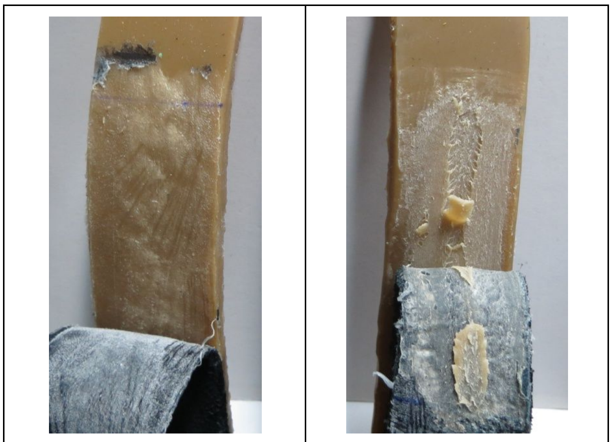
	All treatments	Untreated	TR – chemical treatment	Leather – Mechanical treatment	Leather – primer	TR – chemical treatment Leather – mechanical treatment	Leather – mechanical treatment + primer
Observations							
Fig.	a)	b)	c)	d)	e)	f)	g)

Figure 5 shows that the application of all treatments, namely, on TR the chemical treatment and on leather the application of mechanical treatment and primer, conferred a higher peel strength, were rupture occurs on TR, as shown in the figure a) presented in table 7.
However, as the force increases, at some point TR deformation occurs, and the adhesive joint is not effectively tested, being measured only the elongation of the material, as shown in Figure 7.

Figure 7 - Specimens leather/TR: with deformation of the TR.

In the absence of chemical treatment on TR, the adhesive joint breaks on the interface adhesive / TR as shown in Figures d) and g) of Table 7. In the absence of mechanical treatment on the leather, the adhesive joint breaks by the interface between adhesive and leather, as shown in Figures b), c) and e) of Table 7. When treatment is not applied, the leather/TR adhesive joint behaves in the same way as when only the primer is applied on the leather, or only the chemical treatment on TR, that is, the rupture of the joint occurs by the interface between adhesive and leather.

The application of the chemical treatment on TR promotes anchoring of the adhesive, as shown in Figure 8.



a)	b)

Figure 8 - Specimens leather/TR. a) without chemical treatment on the TR. b) with chemical treatment on TR

Figure 9 shows the load displacement curves in peel testing for various surface treatments for leather/PU adhesive joints.

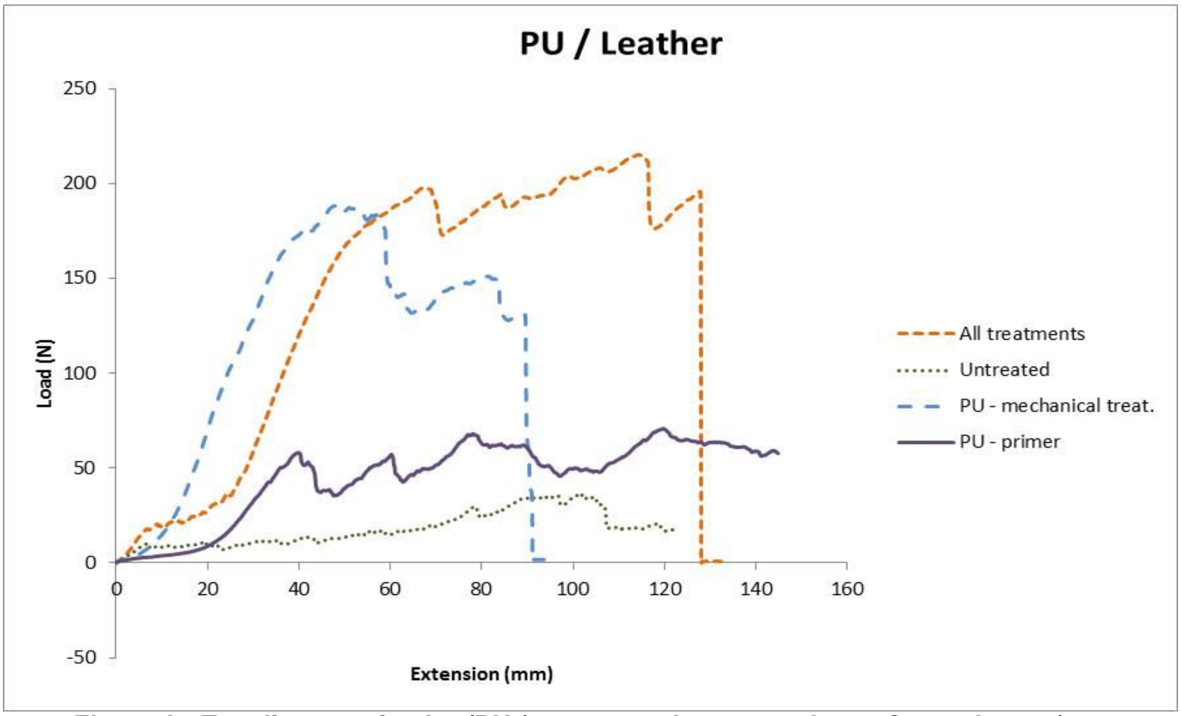


Figure 9 - Tensile tests: leather/PU (representative curve shown for each case)

The maximum strength values and respective standard deviation are shown in Figure 10.

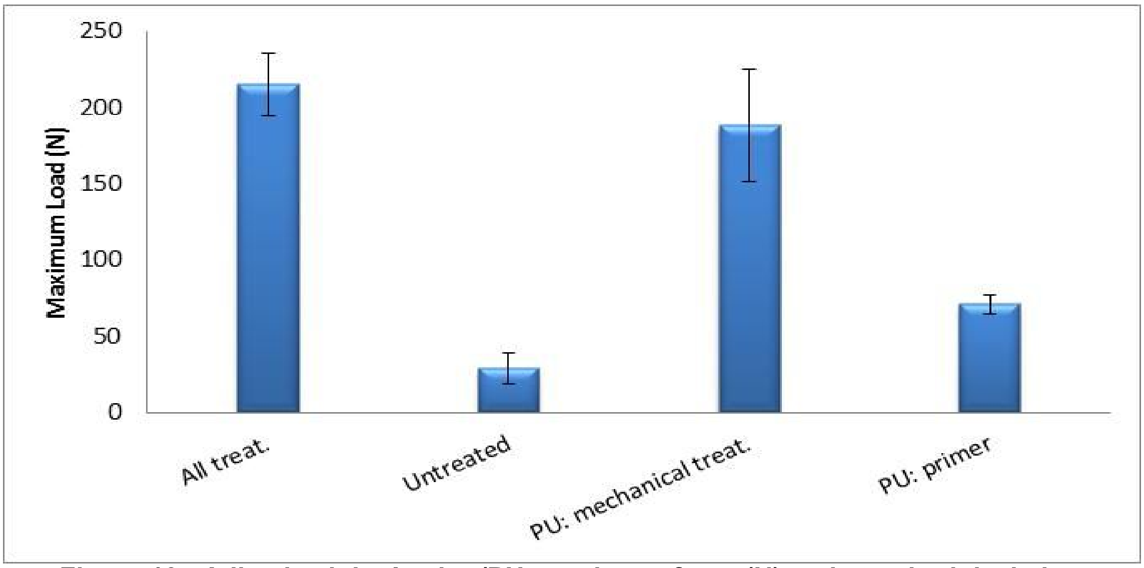


Figure 10 - Adhesive joint leather/PU: maximum force (N) and standard deviation

In Table 8 are identified the types of failure surface of the PU joints, according to their surface treatments.

Table 8 - Adhesive joint leather/PU: types of failure of the peel tests

	All treatments	Untreated	PU – mechanical treatment	PU – primer
Observations				
Fig	a)	b)	c)	d)

Figure 9 shows that when all surface treatments are applied to PU, the rupture at the joint occurs on the PU, and the same was verified when mechanical treatment was applied as shown in Figures a) and c) of Table 8.

When surface treatments are not applied, the rupture occurs through the joint interface between adhesive and PU, and the same is verified when only primer is applied as surface treatment. This is shown in Figures b) and d), respectively.

4. DISCUSSION

With the development of this work it was found that the application of all surface treatments on leather/TR adhesive joint provides the highest failure strength in the peel test. Taking into account that the leather has a surface with low surface tension, if mechanical treatment is not applied, the application of chemical treatment on the TR does not cause any improvement in the joint strength and rupture occurs by the surface layer of the leather. That is, rupture occurs by the interface adhesive / leather. Considering the leather/TR, if only a mechanical treatment is applied on the leather, it is possible to obtain an increase of the peel strength. The primer on the leather works as a reinforcement. The mechanical treatment allows the anchoring of the adhesive and will decrease the thickness of the leather. When primer and mechanical treatment are combined, the peel strength of an adhesive joint is increased.

When applying the chemical treatment on the TR, there is a better anchoring of the adhesive, leading to a more uniform behaviour of the joint. Applying chemical treatment on the TR and mechanical treatment on the leather, allows the adhesive joint to show high values of peel strength, very close to the values obtained when all surface treatments are applied. Since the sample is 30 mm wide and considering the maximum peel strength identified in Figure 6, peel strength per unit width of each adhesive joint was determined and is shown in Table 9.

Table 9 - Adhesive joint leather/TR: peel strength per unit width

Surface treatments	Maximum load (N)	Peel strength per unit width (N/mm)
All treatments	264	8.80
Untreated	17.3	0.58
TR: chemical treatment	17.5	0.58
Leather: mechanical treatment	73	2.43
TR: chemical/Leather: mechan.	227	7.57
Leather: primer	22	0.73
Leather: mechan.+primer	113	3.77

Comparing the values determined in Table 9 and minimum values defined by the standard EN 20344 (5.2), as shown in Table 1, it was found that to obtain conform results for bonding baby shoes it is necessary to apply mechanical treatment on the leather. In women's footwear, in addition to the mechanical treatment, the primer must be applied on the leather. In the men's and children footwear, it is necessary to apply the mechanical treatment in the leather and chemical treatment on the TR. The maximum strength for this case is obtained when applied also at the leather the primer.

In the PU, if only the mechanical treatment is applied, the peel values obtained are high. However, the same cannot be said with if only the primer is applied on PU. Table 10 shows values of the peel strength per unit width of the joint leather/PU.

Table 10 - Adhesive joint leather/PU: peel strength per unit width

Surface treatments	Maximum load (N)	Peel strength per unit width (N/mm)
All treatments	215	7.17
Untreated	29	0.97
PU: mechanical treatment	188	6.27
PU: primer	71	2.37

Comparing the values of Table 10 and the minimum values defined by the standard EN 20344 (5.2), as shown in Table 1, it was found that to obtain conform results of bonding, for baby shoes it is necessary to apply mechanical treatment on the leather and on PU the primer or mechanical treatment can be applied. In the men's women and children footwear, it is necessary to apply the mechanical treatment and primer on leather. On PU the mechanical treatment must be applied, with the maximum strength being obtained when the primer is also applied.

5. CONCLUSIONS

The information obtained in this work allows determining the influence of surface treatments for the manufacture of leather/TR and leather/PU adhesive joints.

It can be concluded that to maximize peel strength of the leather/TR and leather/PU joints it is necessary to apply as surface treatment:

- on TR - chemical treatment,
- on leather - mechanical treatment and primer,
- on PU - mechanical treatment and primer.

However, considering the most demanding footwear, adhesive joints already meet the requirements defined by EN 20344 (5.2) with the application of surface treatments:

- on TR - chemical treatment,
- on leather - mechanical treatment,
- on PU - mechanical treatment.

These conclusions allow manufacturers of footwear to minimize the number of operations in the manufacture of shoes, while still being capable of satisfying the minimum requirements for the sector.

Acknowledgements

To the companies CIPADE, LINOS and Flexsol, the authors gratefully acknowledge the provision of materials required for the manufacture of adhesive joints.

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PAPER 3

SURFACE TREATMENT: THERMOPLASTIC RUBBER AND NATURAL LEATHER

SURFACE TREATMENT EFFECT IN THERMOPLASTIC RUBBER AND NATURAL LEATHER FOR THE FOOTWEAR INDUSTRY

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Abstract

This paper aims to analyze the peel strength of an adhesive joint with various types of surface treatments. In the shoe industry, the adhesive properties are very important to ensure the quality of manufacture of the shoe, thus, to better understand the behaviour of the adhesive joint, it is important to analyze the peel resistance in order to adjust the manufacturing process. In this work, natural leather, thermoplastic rubber (TR) and a non-structural, solvent based, polyurethane adhesive were considered. The influence of the application of chemical and / or mechanical surface treatments on substrates in the peel strength of a T joint were analysed. To characterize the surfaces, several test were considered, including Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscope (SEM) and contact angle measurements. It was found that certain surface treatments are required to obtain an adhesive joint capable of satisfying the minimum strength requirements of the shoes sector.

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Key-words

Peel strength; adhesive joints; footwear; polyurethane adhesive solvent based, thermoplastic rubber, leather, FTIR, SEM, contact angle.

1. INTRODUCTION

In Portugal, the footwear industry has been growing in recent years. This growth is due to the focus on quality, comfort and design of the shoe, providing a large increase in exports. For the manufacture of quality footwear it is important to ensure a robust construction of the shoe, which includes strong and durable adhesive joints. **[1].** For the manufacture of this adhesive joint, one must take into account the need for an adhesive capable of promoting adhesion required by the selected materials **[2-3]**.

The selection of the adhesive and the necessary surface treatment for the production of an optimum adhesive joint depends mainly on the type of material used for the construction of the shoe. Polyurethane (PU) or solvent based policloropreneo (PCP) adhesives are commonly used. For the surface preparation, mechanical treatment, chemical treatment and / or a primer can be used, also chosen depending on the substrate nature **[4-5]**.

This work considers the most complex adhesive joint found in a shoe, the one joining the formed upper to the sole **[6]**. Leather was selected as the material used in the upper. For the sole, thermoplastic rubber (TR) was selected.

The TR soles are based on synthesized polymer blocks, particularly butadiene and styrene, and are formed into the desired shape by a heating process. However, by heating, the connection between butadiene and styrene become more weakened and elastomers may be subjected to a change of shape. Such occurrence is possible because the styrenic monomers are more polar than butadiene and then when styrene is subjected to temperature it becomes liquid.

This characteristic brings advantages, as TR can be subjected to recycling processes **[7]**. Additionally, these soles are characterized as being water resistant, very flexible and resilient. They are also a cheaper material when compared with other materials that exist on the market. TR soles are usually used for making women shoes of good quality. As surface treatment, for TR soles, a chemical treatment is applied, ensuring the cohesive strength of the adhesive joint **[6]**. This treatment allows the chemically modification of the surface to be bonded. In the footwear industry, the halogenated substances are the most commonly used chemical treatment **[7-11]**. The leather uppers used in this work are made from bovine leather. This material is characterized by its comfort, wear resistance, competitive price and wide availability. All these qualities make it suitable for the production of high quality footwear. To ensure good adhesion, leather is usually subjected to a mechanical treatment followed by primer application. The mechanical treatment creates roughening on the substrate surface by increasing the contact area and therefore increasing the number of possible linkages at the interface between the adhesive and the substrate **[11]**. In the footwear industry, the mechanical treatment is the most widely used, with the carding performed using sandpaper **[11-12]**. The primer is applied after carding and works as a surface coating that reinforces the layer that was removed by the mechanical treatment. It is a product based on a polymer solution in organic solvents. This composition is related to the adhesive, but its low viscosity allows the forming of a thin layer on the substrate surface. The primer, when dry, provides a very strong bond with the adhesive, requiring compatibility of the primer with the adhesive **[11-12]**.

To manufacture the adhesive joint, after selection of materials and the respective application of surface treatment, it is necessary to select the type of adhesive and procedure to follow. This work considers a solvent-based PU adhesive. In the footwear industry, in the case of upper / sole bonding, the method of application by brush is used. The reactivation temperature and time are determined by the need to soften the adhesive film and not the sole, enabling rapid development of bond strength. When working with soles that soften at low temperatures, the use of an adhesive is necessary to provide a low temperature required for reactivation, so it might be possible to manufacture the joint by adjusting the time required for the reactivation of the adhesive film **[12]**. Various mechanical properties can be considered important in the manufacture of shoes but the most important is considered to be the peel strength. This paper therefore focuses on the peel strength, performing tests to evaluate the mechanical behaviour of the PU adhesive solvent-based when bonding leather to TR soles, while also taking into account the presence or absence of surface treatments on the substrates. The peel strength is a property which determines the strength required to peel of two materials, where at least one of the substrates is flexible. This test enables to distinguish if an adhesive is fragile or ductile **[12-13]**. It is also a good test to assess the surface treatment.

To quantify this property the peel test was performed in a tensile testing machine, following a test standard. Two standards are used for footwear industry adhesives: ISO 20344:2004 (shoe) **[13]**, EN 1392:1998 (specimen) **[14]**.

This paper follows a previous study of Paiva et al. **[15]** about PU/leather, but in this case TR was chosen as the sole, to evaluate the bonding properties of soles, where ISO 20344:2004 standard was followed. This standard allows the determination of the peel strength per unit width, which is the average load per unit width needed to lead to rupture. The load is applied at an angle between 90° and 180° in relation to the joint, depending on the flexibility of the substrate. This norm establishes the minimum values to consider for difficult bonding. Table 1 refers to the values required for joining the upper to the sole.

Table 1: Reference values of adhesion upper / soles, according to standard EN 20344

Shoes	Peel Strength per unit width (upper/sole)
Baby	≥ 2 N/mm
Child	≥ 4 N/mm
Woman	≥ 3 N/mm
Man	≥ 4 N/mm

EN 1392:1998 determines the test method for obtaining the bond strength at an angle of 180º, but using the materials in the shape of a specimen, as shown in Figure 1 **[16]**.

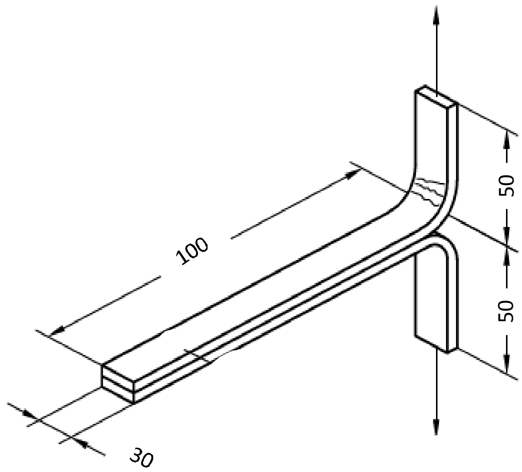


Figure 1: Adhesive joint for peel test (dimensions in millimetres)

2. EXPERIMENTAL

The experimental portion of this work consisted on the analysis of the peel strength of TR/leather joints. Also included in this section is an analysis of the surface materials, without and with surface treatments, by FTIR, SEM and contact angle measurements.

2.1 Materials

For the elaboration of this work, the TR selected was TTSC TR-2531-80C (LINOS - Componentes para calçado, L.A., Santa Maria da Feira, Portugal). In Table 2 it is possible to verify the characteristics of the TR used in this work; this information is provided by the manufacturer of the sole (technical datasheet of the material).

Table 2 - Characteristics of the TR

Characteristics	Method	units	Sonaflex TTSC-2531-80C
Density	ASTM D792	g/cm^3	0.92 – 0.98
Hardness	DIN 53505	Shore A	77 – 83
Tensile	DIN 53504	MPa	≥ 4
Elongation at rupture	DIN 53504	%	≥ 300
Abrasion resistance	DIN 53516	mm^3	≤ 250
Flexion resistance	BS 5131:2.1 (150000 cycles)	mm/Kc	< 0.1

As a halogenate for TR, Halinov 2190 (CIPADE – Indústria e Investigação de Produtos Adesivos, S.A., São João da Madeira, Portugal) was used. In Table 3 it is possible to verify the characteristics of the Halinov 2190; this information is provided by the manufacturer (technical datasheet of the material).

Table 3 **- Characteristics of the** Halinov 2190

Characteristics	Units	Halinov 2190
Density	g/cm^3	0.87 – 0.93
Drying time	hour	min.1
Active chlorine	%	24 – 30

As a primer for the leather the Plastik 6271 was selected (CIPADE – Indústria e Investigação de Produtos Adesivos, S.A. São João da Madeira, Portugal).

Plastik 6275 (CIPADE – Indústria e Investigação de Produtos Adesivos, S.A., São João da Madeira, Portugal), a solvent based PU was used as the adhesive, which has a sufficient viscosity for the effective wetting and is able to penetrate into the cavities created by the mechanical treatment on the substrate. Table 4 shows the characteristics of the primers and the adhesive used. These values were supplied by the manufacturer (technical datasheet of the products).

Table 4 **- Characteristics of the** primers and adhesive

Characteristics	Units	Plastik 6275	Plastik 6109	Plastik 6271
Viscosity	cPs	3500-4000	100 – 200	250 – 300
Solids	%	15 – 19	6 – 10	18 – 21
Density	g/cm^3	0.82 – 0.88	0.83 – 0.89	0.85 – 0.91
Drying time	min.	10 – 15	60	5 – 20
Reactivation temperate	^{0}C	70	-	-

2.2 Experimental Techniques

2.2.1 Surface Treatments

For the application of the surface treatment one must take into account the materials which are intended to be bonded. This work took into account the following points:

- *Variables for the surface treatment of leather*

a. The leather substrates were subjected to a mechanical treatment;
b. The primer (Plastik 6271) was applied and allowed to dry for 5 to 20 minutes at room temperature;

- *Variables for TR surface treatment*

a. The TR substrate was subjected to a chemical treatment (Halinov 2190) and allowed to dry at least 1 hour at room temperature;

- *Procedure for the manufacture of the peel joint*

a. The adhesive, Plastik 6275, was applied in both substrates and allowed to dry for 10 to 15 minutes at room temperature;

b. The adhesive films were activated by Infrared (IR) radiation at about 70° C for 6 seconds;
c. The substrates, were bonded in the desired position, as seen in Figure 2;
d. The adhesive joint was subjected to 2 to 4 bar of pressure for 4 to 5 seconds.

For the mechanical treatment, a P24 aluminium oxide abrasive cloth was used.

The adhesive joints, after being pressed, were stored in standard conditions (23 °C, 50% relative humidity) during 24h, in order to ensure the complete cure of the adhesive. Only then they were subjected to the peel test.

2.2.2 Fourier Transform Infrared Spectroscopy (FTIR)

The IR spectra of the treated samples were obtained using a PerkinElmer Spectrum Two (Llantrisant, UK).

The attenuated total multiple reflection technique (ATR) was used to analyse the chemical modifications produced in about 5 μm depth on the materials surface.

The sample was directly placed on the diamond ATR top plate mounted in the sample beam of the spectrometer. The measurements were completed within 30 seconds and the ATR spectrum was obtained. Two hundred scans were obtained and averaged with a resolution of 4 cm^{-1}. The incident angle of the IR radiation was 45°.

The IR spectrum obtained are graphs of infrared light absorbance (A) on the vertical axis and wavelength on the horizontal axis. The units of the wavelength are reciprocal centimeters (cm^{-1}).

2.2.3 Scanning Electron Microscopy (SEM)

Scanning electron microscope (SEM) analyses were produced in a JEOL JSM 6301F/ Oxford INCA Energy 350/Gatan Alto 2500 microscope (Tokyo, Japan). This equipment was used to analyse the external surface modifications on the TR and on the natural leather produced by the treatments. The samples were secured on copper mounts by means of a silver paste and were gold-coated before the SEM micrographs were obtained.

2.2.4 Contact Angle Measurements

Contact angle measurements were carried out using the sessile drop method. The adhesive in study Plastik 6275 was chosen as the test liquid. Measurements were obtained at 25°C. Single drops of Plastik 6275 were placed on the surface of the TR and leather untreated and treated, and the contact angle for all surfaces was measured. The values obtained for TR and the leather were reproducible, at least three measurements on the same sample were obtained with an error less than +/- 3 degrees.

2.2.5 Peel test

In this work, for the manufacture of the joint, it was decided not to study the full sole and upper combination, but instead smaller peel specimens were manufactured.

The adhesive joint studied was composed of two substrates (150mm x 30mm) glued together in an area of 100mm x 30mm, as shown in Figure 2.

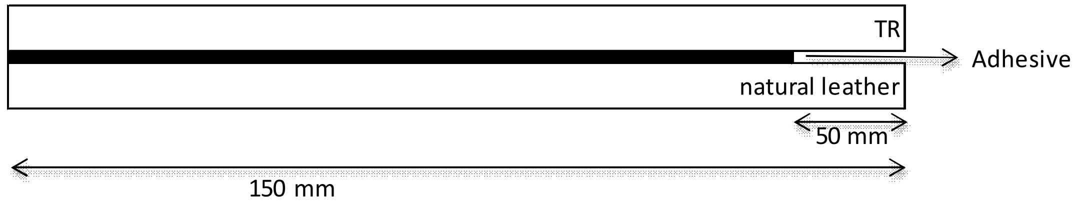


Figure 2 – Test piece geometry

In the production of the adhesive joints, taking into account the material under study, the surface treatments were considered as variables, in order to be able to identify their importance in the peel strength. Therefore, the first step was making an application of all treatments commonly used in the footwear industry, followed by the manufacture of an adhesive joint without any surface treatment. In addition, joints were fabricated where only one of the treatments was performed for comparison purpose. Other combinations were done in order to examine the effect of treatments. For the preparation of this work, for leather/TR joints, the test plan identified in Table 5 was followed.

Table 5 **- Test plan for leather/TR specimens**

Mat.	**Surface treatment**	**Surface treatment combinations**						
		1	2	3	4	5	6	7
TR	chemical	X		X		X		
Leather	mechanical	X			X	X		X
	primer	X					X	X

24 hours after the manufacture of the adhesive joint, the peel test was performed in a testing machine at a speed of 50 mm/min. The results are expressed as load (N) versus displacement (mm). The peel strength per unit of

width was determined by the ratio between the maximum force and the width of the overlap joint. Three adhesive joint specimens for each test were considered.

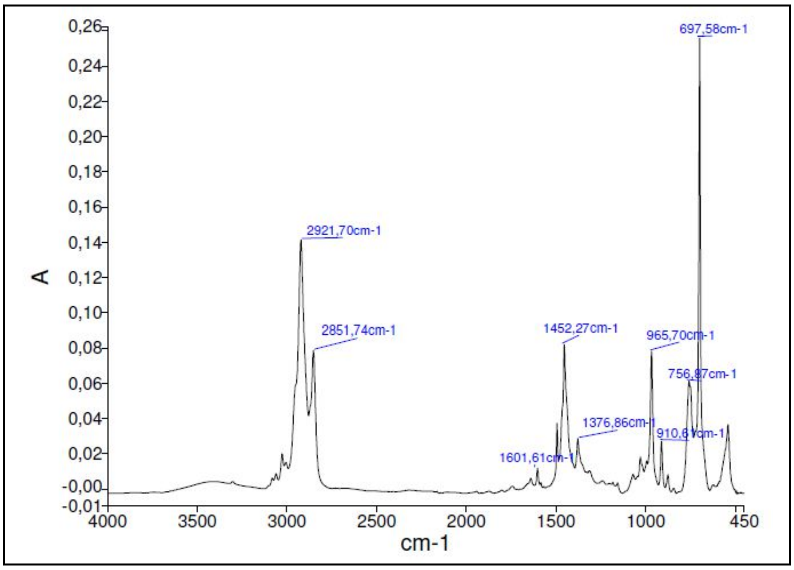
The tensile machine used was an Instron (Norwood, MA, USA), model 3367, with load cell of 30kN.

3. RESULTS

The following sections list the test results and their discussion, the chemical and physical characterization of materials with and without treatment as well as the behaviour of joints when subjected to peel tests.

3.1 Chemical characterization of the materials surfaces

Figure 3 shows the spectrum obtained for the TR surface without any surface treatment.



*Vertical axis: A – absorbance. Horizontal axis: Wavelength (cm^{-1})

Figure 3 - ATR-IR spectrum of TR without surface treatment.

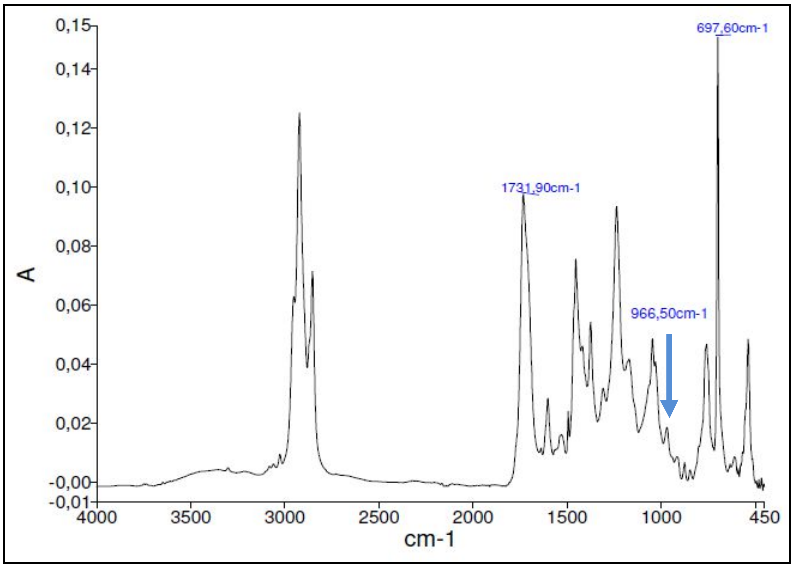
Analysing the spectrum in Figure 3 the presence of absorption bands related to butadiene and styrene can be verified. The absorption bands corresponding to each of the above compounds are listed in Table 6:

Table 6 – Functional groups and absorption bands of butadiene and styrene

	Functional group	Absorption bands (cm^{-1})
Butadiene	$-CH_2$, CH_3 stretching	2921.70; 2851.74
	$-CH_2$ scissoring	1452.27
	$-CH_2$ twisting	1376.86
	trans-1,4-C=C	965.70
Styrene	C-C aromatic group stretching	1601.61
	C-H stretching	3026.70
	C-H out-of-plane deformation of vinyl group	697.58; 756.87; 910.61

Figure 4 shows the ATR-IR spectrum obtained for the TR surface after halogenation. Such surface treatment is commonly used for the footwear industry to bond TR soles with natural leather, using adhesives based on polyurethane to produce the adhesive joint. In this case, the chlorine atoms present in the molecular structure of the halogenated compound are responsible for promoting strong molecular interactions with the same substrates.

The ATR-IR spectrum represented in Figure 4 shows the chemical modifications by halogenation (Halinov 2190) of the TR surface.

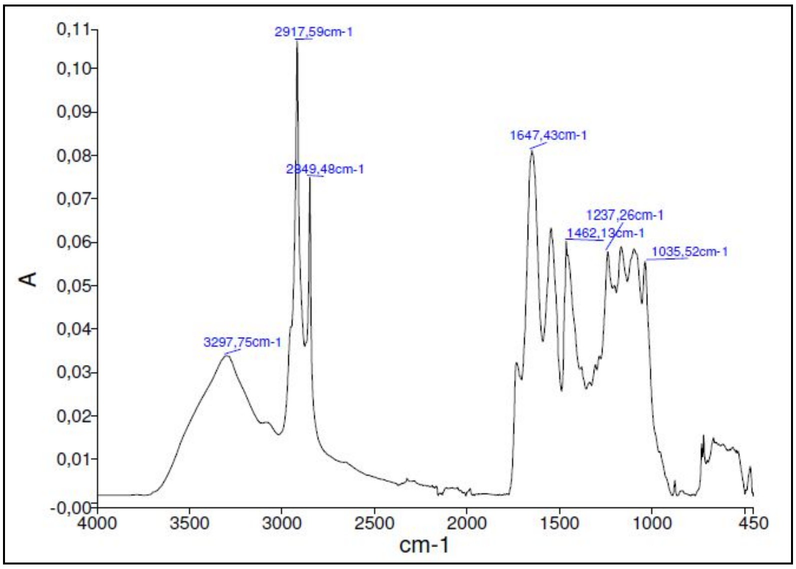


*Vertical axis: A – absorbance. Horizontal axis: Wavelength (cm^{-1})

Figure 4 - ATR-IR spectrum of TR with surface treatment (halogenation).

Figure 4 shows that with halogenation of the TR, substantial chemical changes of its surface can be obtained. Such modifications can be evidenced by the appearance of new absorption bands compared to the surfaces of untreated rubber. Among these changes, the effect is the appearance of the characteristic absorption bands of chlorine (C-Cl) in 697,60 cm^{-1}. The band at 1726.12 cm^{-1} demonstrates that oxidation of the rubber surface occurred, where C=O groups are created as a consequence of those oxidation. On the other hand, comparing with the spectrum of the untreated TR (Figure 3), the intensity of the IR bands due to C=C is decreased (910.61, 965.70, 757.40 cm^{-1}).

The ATR-IR analysis of the surface of the natural leather without treatment (Figure 5) indicates that it presents essentially the absorption bands related to the polypeptide chains of collagen: NH stretching (3297.75 cm^{-1}), CH_2 and CH_3 stretching (2917.59, 2849.48 cm^{-1}), C = O stretching (1647.43 cm^{-1}), N-H stretching (1462.13 cm^{-1}), C-N stretching (1237.26 cm^{-1}), C-O stretching (1035.52 cm^{-1}). Figure 5 refers to the main absorption bands for untreated natural leather.



*Vertical axis: A – absorbance. Horizontal axis: Wavelength (cm^{-1})

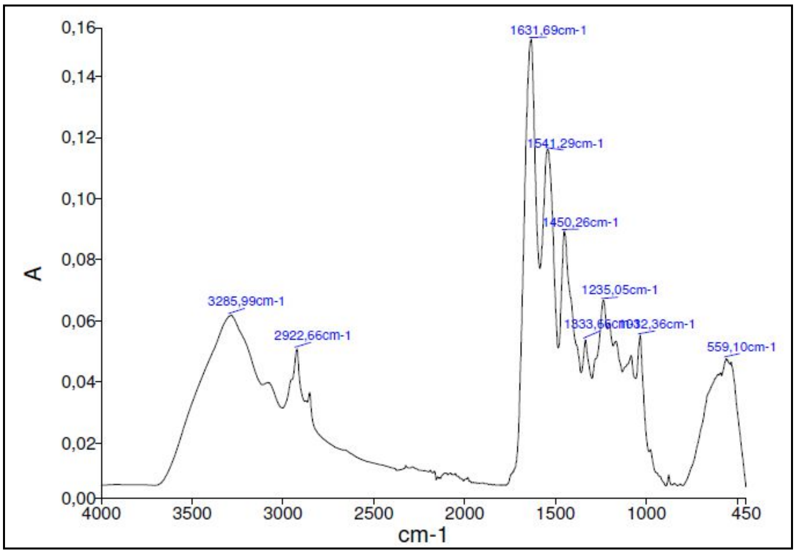
Figure 5 - ATR-IR spectrum of natural leather untreated

Table 7 shows the assignment of the most relevant absorption bands for untreated natural leather.

Table 7 – Functional groups and absorption bands of natural leather

Functional group	Absorption bands (cm^{-1})
O-H stretching	3000 – 3500
N-H stretching	3297.75
$-CH_2$, CH_3 stretching	2917.59, 2849.48
C=O stretching	1647.43
N-C=O stretching	1544.11
CH_2, CH_3 stretching	1462.13
C-N stretching	1237.26
C-O stretching	1035.52

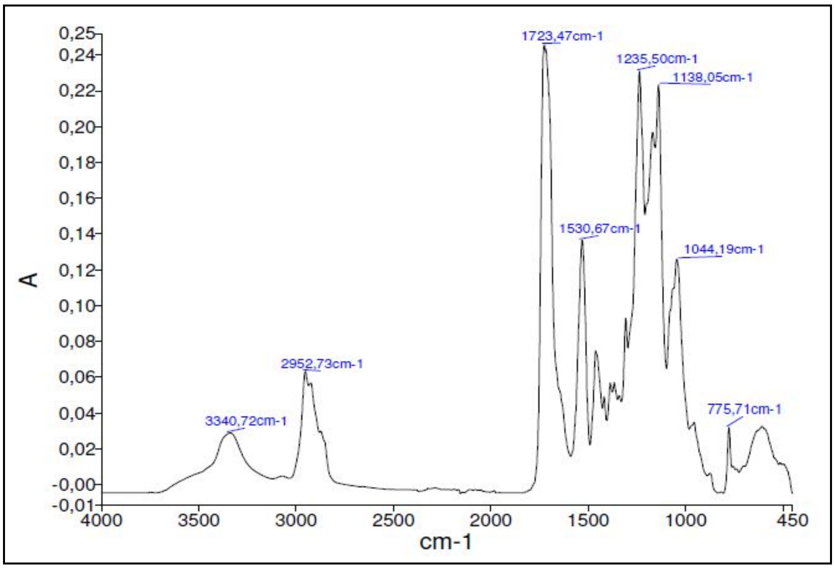
For bonding the TR to natural leather, an adhesive based on polyurethane (Plastik 6275) was applied. In this case the application of mechanical (carding) and a primer treatment on the leather surface is required. The primer applied on the leather (Plastik 6271), has the same chemical nature of the adhesive and will regulate the penetration of the adhesive into the substrate, whereas the leather is extremely porous, promoting in this way the chemical compatibility between the substrate and adhesive. Figures 6 and 7 present the main chemical changes on the leather surface resulting from the mechanical treatment and primer, respectively.



*Vertical axis: A – absorbance. Horizontal axis: Wavelength (cm^{-1})

Figure 6 - ATR-IR spectrum of natural leather with mechanical treatment.

Figure 6 shows that with mechanical treatment of the natural leather, changes can be observed; the decrease of characteristic absorption bands, C-H stretching (2917.59, 2849.48 cm^{-1}), and, on the other hand, the increase of the intensity of the bands due to C = O stretching (1647.43 cm^{-1}) and N-H stretching (1544.11 cm^{-1}).



*Vertical axis: A – absorbance. Horizontal axis: Wavelength (cm^{-1})

Figure 7 - ATR-IR spectrum of natural leather with mechanical treatment and primer.

Analysing Figure 7, the absorption bands correspond to the primer. Table 8 shows the most relevant absorption bands of the natural leather with mechanical treatment and primer.

Table 8 – Functional groups and absorption bands of natural leather with mechanical treatment and primer

Functional group	Absorption bands (cm^{-1})
N-H stretching	3340.72
C-H stretching	2952.73
C=O stretching	1723.47
N-H bending and N-C=O symmetric stretching	1530.67
C-N stretching	1235.50
C-O stretching	bands at 1100 to 1235
N-H out-of-lane deformation	775.71

3.2 Topological characterization of the materials surfaces

Figures 8 present SEM micrographs obtained for TR substrates with and without surface treatment, increased 30x and 100x, respectively.

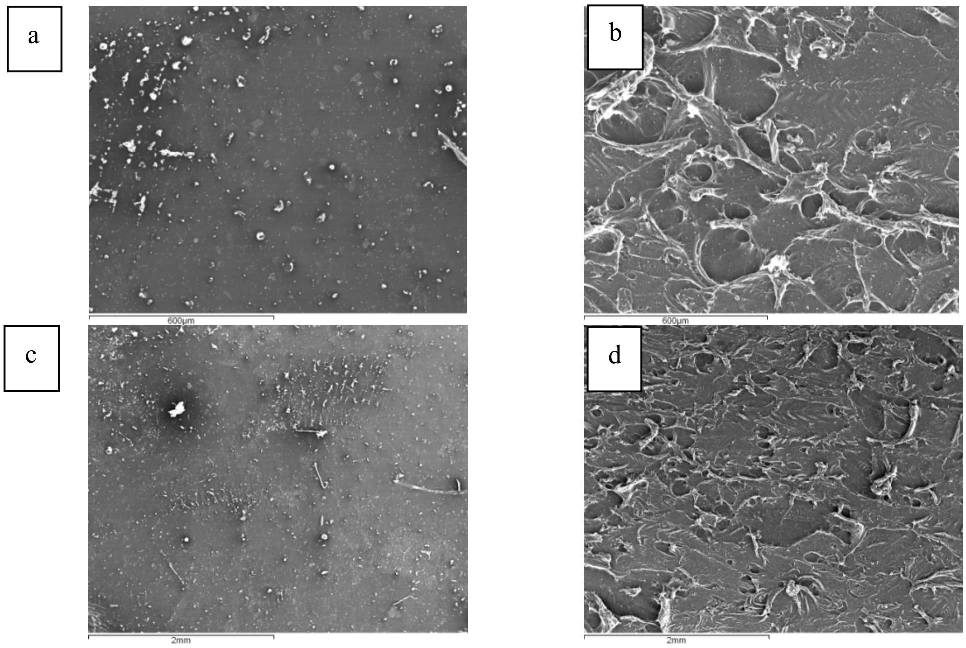


Figure 8 - **SEM micrographs (30x) of TR: a) untreated (30x), b) with chemical treatment (30x), c) untreated (100x), d) with chemical treatment (100x)**

It can be observed that the surface of TR without surface treatment showed a smooth appearance, quite different from that presented by treated TR. The Figure 8 show the relatively rough surface caused by the chlorination that creates holes on the surfaces on the TR. This chlorination reaction on the surface of the rubber by the action of halogenated compound is processed very quickly, promoting efficient adhesion between TR and polyurethane adhesives.

As for TR, the morphological changes introduced on the leather surface due to application of specific surface treatment were also evaluated. Figures 9 and 10 represent the SEM micrographs obtained for leather substrates with and without surface treatments, increased 30x and 100x, respectively.

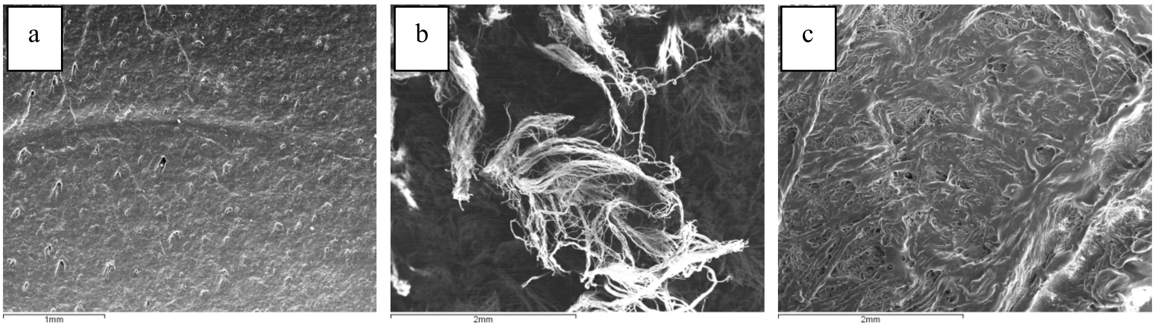


Figure 9 – SEM micrographs (30x) of natural leather: a) untreated, b) with mechanical treatment, c) with mechanical treatment and primer

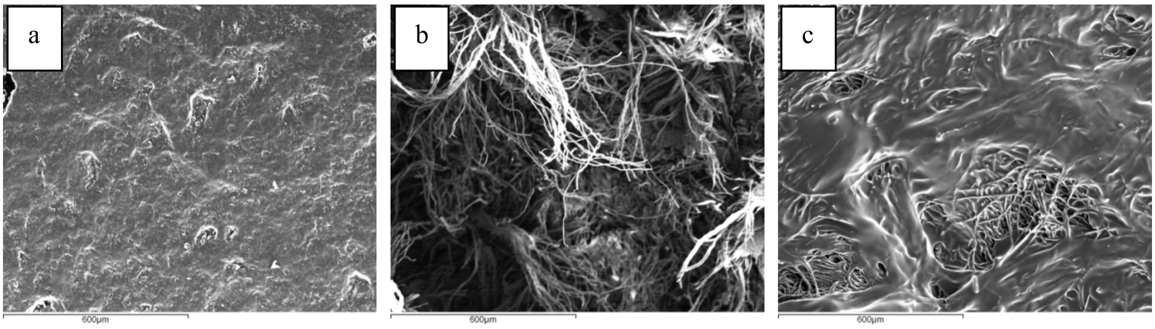


Figure 10 – SEM micrographs (100x) of natural leather: a) untreated, b) with mechanical treatment, c) with mechanical treatment and primer

As can be seen in Figures 9 and 10, the surface of the leather, after suffering surface treatment (mechanical treatment, combination of mechanical treatment with primer), presents a higher irregularity than that presented by untreated leather. With a magnification of 100x (Figure 10) it can also be observed that the mechanical surface treatment, caused by the removal of the weak grain layer of the leather, results in increased exposure of collagen fibres at the surface. When the primer in applied (Figure 9 c, Figure 10 c), the collagen fibres become more compacted on the surface.

Regarding the differences provided by the surface due to the application of the primer Plastik 6271, the appearance of a solid layer on the surface may be observed on Figure 10.

3.3 Contact angle characterization of the materials surfaces

The wettability of the untreated and treated TR and natural leather surface was characterized by contact angle measurements. Table 9 shows the contact angle values obtained after placing drops of Plastik 6275 on the untreated and treated TR and natural leather surfaces, as it can be seen on the Figure 11 and 12.

Table 9 – Contact angle values (Plastik 6275) on TR and natural leather surface untreated and treated

	Untreated	Treated	
natural leather	120	(1)	109
		(2)	94
TR	107		84

(1) Leather with mechanical treatment surface
(2) Leather with mechanical treatment surface and primer

The untreated natural leather shows a high contact angle (120 degrees) due to the poor wettability. The mechanical treatment produce a decrease in contact angle values on the natural leather surface (109 degrees), caused by the increased of the surface energy. And the application of primer decreases the contact angle even more (94 degrees) because of its compatibility with the adhesive (Plastik 6275).

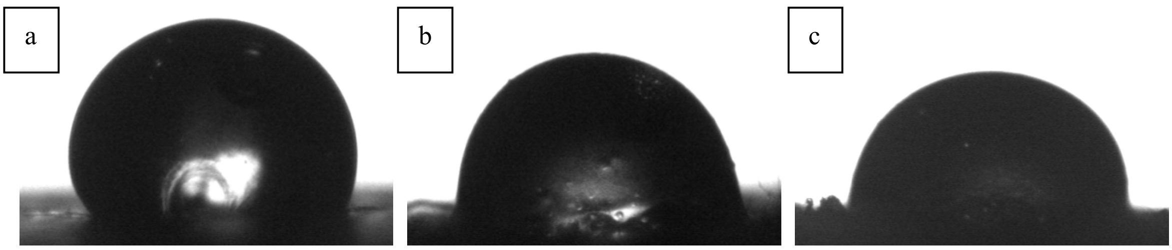


Figure 11 – Drop of Plastik 6275 on leather surface: a) untreated, b) with mechanical treatment, c) with mechanical treatment and primer

The untreated TR shows a high contact angle (107 degrees) due to the poor wettability. The treatment produces a decrease in contact angle values on the TR rubber surface (84 degrees), caused by the increased of the surface energy.

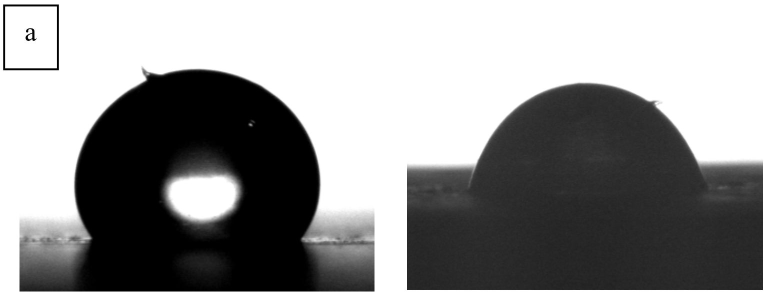


Figure 12 – Drop of Plastik 6275 on TR surface: a) untreated, b) with chemical treatment

3.4 Analysis of the peel strength

Figure 13 shows the load-displacement curves for different surface treatments of the adhesive joints using leather/TR.

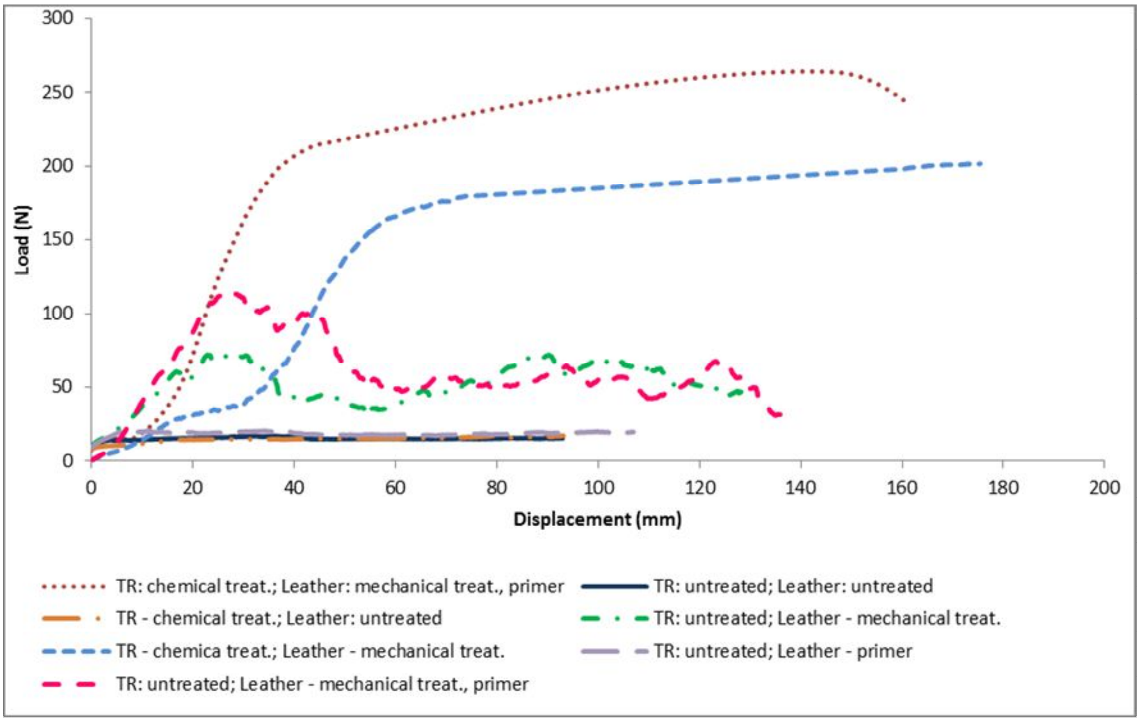


Figure 13 - Tensile tests: leather/TR (representative curve shown for each case)

The maximum load per unit width values and standard deviation associated with each test are shown in Figure 14.

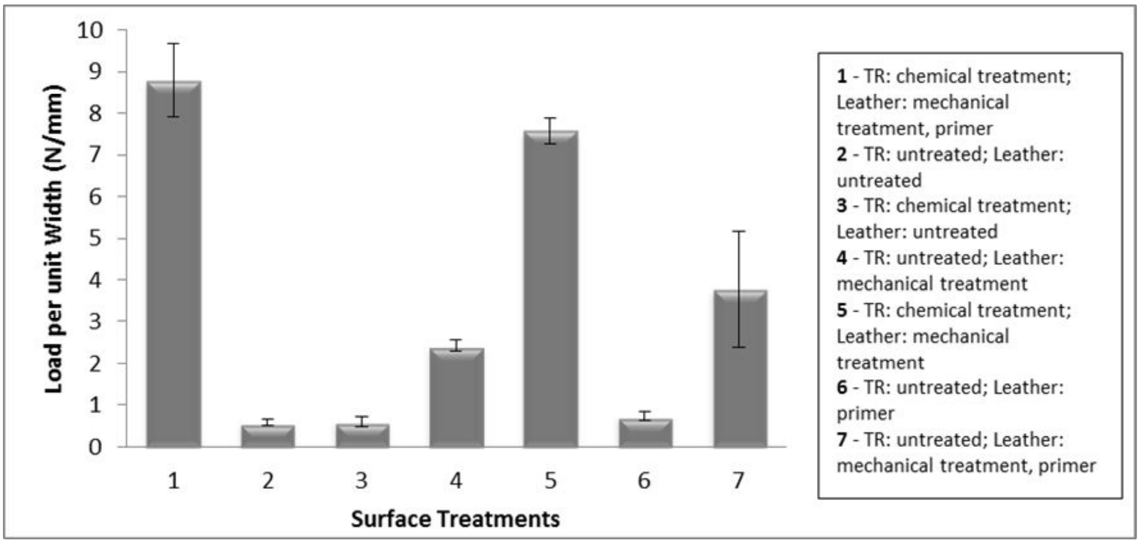


Figure 14 – Peel strength: TR / leather for various surface treatment combinations

Table 10 shows the different types of failure identified on the tested joints, divided according to their treatment.

Table 10 – Adhesive joint leather/TR: types of failure of the peel tests

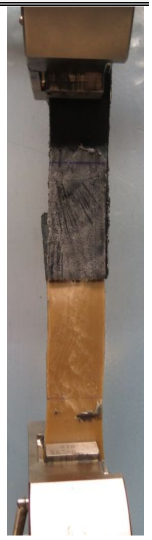
	Surface treatment combinations (see Table 4)						
	1	**2**	**3**	**4**	**5**	**6**	**7**
Observations							

Figure 13 shows that the application of all treatments, namely, on TR the chemical treatment and on leather the application of mechanical treatment and primer, conferred the highest peel strength, where rupture occurs on TR, as shown in Table 10. However, as the force increases, at some point TR deformation occurs, and the adhesive joint is not effectively tested, only the elongation of the TR material being measured, as shown in Figure 15.

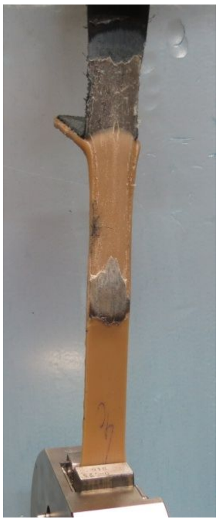
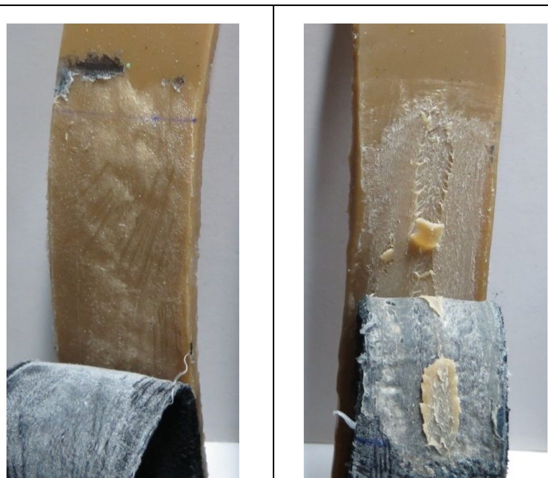


Figure 15 - Specimens leather/TR: with deformation of the TR.

In the absence of chemical treatment on TR, the adhesive joint breaks on the interface adhesive / TR as shown in Table 10. In the absence of mechanical treatment on the leather, the adhesive joint breaks by the interface between adhesive and leather. When treatment is not applied, the leather/TR adhesive joint behaves in the same way as when only the primer is applied on the leather, or only the chemical treatment on TR, that is, the rupture of the joint occurs at the interface between adhesive and leather.

The application of the chemical treatment on TR promotes anchoring of the adhesive, as shown in Figure 16.



a)	b)

Figure 16 - Specimens leather/TR. a) without chemical treatment on the TR. b) with chemical treatment on TR

4. DISCUSSION

The FTIR spectrum allowed us to detect functional groups present on the material surfaces. Comparing the TR untreated surface with the same surface after application of the chemical treatment, the chemical composition of this material after chlorination can be verified. On the leather, comparing the untreated surface of the materials with the application of the mechanical treatment, it can be verified that the removal of the outer layer promotes the exposure of collagen fibres ("corium") according to the changes observed on the bands. Analysing the spectrum of the leather (Figure 7) treated with primer it can be concluded that the bands seen correspond mainly to the primer.

During the course of this work it was found that the simultaneous application of all surface treatments on leather/TR provides the highest failure strength in the peel test. Taking into account that the leather has a low surface tension, if mechanical treatment is not applied, the application of chemical treatment on the TR does not cause any improvement in the joint strength and joint failure occurs at the surface layer of the leather. If only a mechanical treatment is applied on the leather, it is possible to obtain an increase of the peel strength. The primer on the leather works as a reinforcement. The mechanical treatment allows the anchoring of the adhesive. When primer and mechanical treatments are combined, the peel strength increased.

When applying the chemical treatment on the TR, there is a better anchoring of the adhesive, leading to a more uniform behaviour of the joint. Applying chemical treatment on the TR and mechanical treatment on the leather, allows the adhesive joint to show high values of peel strength.

The contact angle analysis confirms the influence of the surface treatment on the TR and on the leather, because it increases the wettability of the surfaces.

Comparing the values of obtained in Figure 13 and the minimum values defined by standard EN 20344, as shown in Table 1, it was found that to obtain conform results of bonding, for baby shoes it is necessary to apply at least on the leather the mechanical treatment. For the men, women and children footwear, it is necessary to apply a chemical treatment on the TR and on the leather the mechanical treatment must be applied, with the maximum strength being obtained when the primer is also applied.

5. CONCLUSIONS

The information obtained in this work allows determining the influence of surface treatments for the manufacture of leather/TR adhesive joints. It can be concluded that to maximize the peel strength of the leather/TR joints it is necessary to apply as surface treatment:

- on TR - chemical treatment,
- on leather - mechanical treatment and primer.

However, considering the most demanding footwear, adhesive joints already meet the requirements defined by EN 20344 with the application of surface treatments:

- on TR - chemical treatment,
- on leather - mechanical treatment.

These conclusions allow manufacturers of footwear to minimize the number of operations in the manufacture of shoes, while still being capable of satisfying the minimum requirements for the sector.

The peel strength of the adhesive joint was monitored after 72 hours, however, PU adhesives are known for their high durability. The durability of the PU adhesive is compromised when the adhesive joint is subjected to high temperatures, when the footwear is subject to improper condition for which it was designed or when the joint is not properly manufactured.

Acknowledgements

CIPADE, LINOS and Flexsol materials required for the manufacture of adhesive joints.

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PAPER 4

SURFACE TREATMENT: POLYURETHANE AND NATURAL LEATHER

EFFECT OF THE SURFACE TREATMENT IN POLYURETHANE AND NATURAL LEATHER FOR THE FOOTWEAR INDUSTRY

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Abstract

This aim of this paper is to analyse the peel strength of an adhesive joint with various types of surface treatments in order to contribute to the research and development of adhesives for the footwear industry. In the shoe industry, the adhesive properties are very important to ensure the quality of manufacture of the shoe. To better understand the behaviour of the adhesive joint, it is important to measure the peel resistance of the adhesive and use it to adjust the manufacturing process. For this work, joints were manufactured using natural leather, polyurethane (PU) and a solvent based polyurethane non structural adhesive. The influences of the application of physical surface treatments and/or primer on substrates in the peel strength of a T joint were analyzed. Several tests were used to characterize the surfaces of the substrates, including Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscope (SEM) and contact angle measurements. It was found that

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certain surface treatments are required to obtain an adhesive joint capable of satisfying the minimum requirements of the shoes manufacturing sector.

Key-words

Peel strength; adhesive joints; footwear; polyurethane adhesive solvent based, polyurethane, leather, FTIR, SEM, contact angle.

1. INTRODUCTION

In Portugal, the footwear industry is increasingly characterized by quality, comfort and beauty of its models. Hence, there has been an increase in exports, evident over the past years. While comfort is determined by the selection of materials and the shoe design, quality is determined by the construction of the shoe and is also a reflection of the materials used and the manufacturing process of the adhesive joint **[1].** For the manufacture of the adhesive joint, one must take into account the need for an adhesive capable of promoting adhesion required by the selected materials **[2-3]**.

The selection of an optimum adhesive for the adhesive joint is not always an easy task because the materials differ and, in many cases, the materials selected for construction of a shoe model are subjected to surface treatments, which increases the complexity of the manufacturing process but provide a better union of the materials **[4-5]**.

For the manufacture of footwear it is necessary to take into account the following operating procedures: cutting, sewing, fitting and finishing **[6]**. For the preparation of this work the most demanding type adhesive joint was considered. The joint described in this paper is part of the fitting procedure, which adjusts the upper to the form of the shoe and proceeds to glue it to the sole **[6-7]**.

For the elaboration of this work, leather was selected as the material to use in the upper. For the sole, polyurethane (PU) was selected.

PU soles are a combination of polyol with isocyanate, although for production it may also be necessary to apply additives, in particular catalysts and pigments **[8]**. After mixing these substances, a reaction occurs which enables synthesis of the polyurethane compound. This mixture is made and then immediately subjected to injection moulding, allowing to mould a sole in the desired shape **[9-10]**. This type of sole is characterized by its durability, high resistance to wear, light weight, abrasion-resistance, ease to pigment, good thermal insulation, good flexibility at low temperatures and excellent resistance to oils **[9], [11], [12]**. As a thermosetting material it does not soften when exposed to heat. All these properties allow the manufacture of good quality shoes **[13]**. The PU soles have wide application in sports shoes, safety shoes, men's and women footwear that require a boldest design, among others. During production, PU soles are coated with a release agent to facilitate its removal from the mould **[8], [14]**. The PU soles are then subjected to surface treatments **[15]**. The footwear industry uses more than one treatment, starting with mechanical carding which is followed by application of a primer **[16-19]**. On the leather based uppers, a mechanical treatment is performed, followed by the application of a primer. This treatment creates mechanical roughening on the substrate surface by increasing the contact area and therefore increasing the number of possible linkages at the interface between the adhesive and the substrate **[20]**. In the footwear industry, the mechanical treatment is the most widely used, with the carding performed using sandpaper **[13]**. The primer also works as a surface pre-treatment and consists in a polymer solution in organic solvents. This composition is related with the adhesive, but with low viscosity, forming a thin layer on the substrate. The primer, when dry, provides a very strong bond with the adhesive, requiring compatibility of the primer with the adhesive **[13]**. In the footwear industry, various methods are used depending on the application operation. In the case of bonding upper / sole, the method of application by brush is used.

The reactivation temperature and time are determined by the need to soften the adhesive film and not the sole, enabling rapid development of bond strength. When working with soles that soften at low temperatures, the use of an adhesive is necessary to provide a low temperature required for reactivation, so it might be possible to manufacture the joint by adjusting the time required for the reactivation of the adhesive film **[20].** Various mechanical properties can be considered important in the manufacture of shoes but the most important is considered to be the peel strength. This paper therefore focuses on the peel strength, performing tests to evaluate the mechanical behaviour of the PU adhesive solvent-based when bonding leather to PU soles, while also taking into account the presence or absence of surface treatments on the substrates. The peel strength is a property which determines the strength required to peel off two materials, where at least one of the substrates is flexible. This test enables to distinguish if an adhesive is fragile or ductile **[21]**.

To quantify this property the peel test was performed in a tensile testing machine, following a test standard. Two standards are used for footwear industry adhesives: ISO 20344:2004 (shoe) **[22]**, EN 1392:1998 (specimen) **[23]**.

ISO 20344:2004 is designed to evaluate the bonding properties of soles where adhesion is measured by determining whether or not it is acceptable for the desired effect. This standard allows to obtain the peel strength per unit width, which is the average load per unit width, applied at an angle between 90° and 180°, depending on the flexibility of the substrate, in relation to the joint, needed to lead to rupture. In the footwear industry, independently of the type of materials used, to ensure its durability, it is necessary for adhesive joints fulfilling certain specifications defined by EN 20344, which establishes the minimum values to consider for difficult bonding. Table 1 refers to the values required for joining upper/sole.

Table 1: Reference values of adhesion upper / soles, according to standard EN 20344

Shoes	Peel Strength per unit width (upper/sole)
Baby	≥ 2 N/mm
Child	≥ 4 N/mm
Woman	≥ 3 N/mm
Man	≥ 4 N/mm

EN 1392:1998 determines the test method for obtaining the bond strength at an angle of 180º, but using the materials in the form of specimen, as shown in Figure 1 **[24]**.

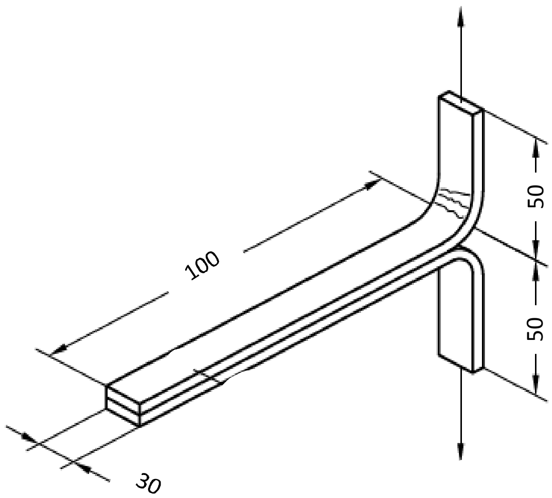


Figure 1: Adhesive joint for peel test (dimensions in millimetres)

2. EXPERIMENTAL

The experimental portion of this work consisted of the analysis of peel strength in the single lap joint, subjected to tensile loading. Also included in this section is an analysis of the surface materials, without and with surface treatments, by FTIR, SEM and contact angle measurements.

2.1 Materials

For the elaboration of this work, the PU selected was Flexsol 486 (*Flexsol – Indústria de PU, Ltd., Santa Maria da Feira, Portugal*). In Table 2 it is possible to verify the characteristics of the PU used in this work; this information is provided by the manufacturer of the sole (technical datasheet of the material).

Table 2 - Characteristics of the PU

Characteristics	Method	Units	PU 486
Density	DIN 53420	g/cm^3	0.55
Hardness	DIN 53505	Shore A	57
Tensile	DIN 53504	MPa	4.8
Elongation at rupture	DIN 53504	%	457
Abrasion resistance	DIN 53516	mm^3	298
Tear strength	DIN 53507	N/mm	8.9
Flex fatigue resistance	DIN 53543	cycles	100000

As a primer for PU, Plastik 6109 (*CIPADE – Indústria e Investigação de Produtos Adesivos, S.A., São João da Madeira, Portugal*) was used, and as a primer for the leather the Plastik 6271 was selected (*CIPADE – Indústria e Investigação de Produtos Adesivos, S.A., São João da Madeira, Portugal*).

Plastik 6275 (*CIPADE – Indústria e Investigação de Produtos Adesivos, S.A., São João da Madeira, Portugal*), a solvent based PU was used as the adhesive, which has a sufficient viscosity for the effective wetting and is able to penetrate into the cavities created by the mechanical treatment on the substrate. Table 3 shows the characteristics of the primers and the adhesive used. These values were supplied by the manufacturer (technical datasheet of the products).

Table 3 - Characteristics of the primers and adhesive

Characteristics	Units	Plastik 6275	Plastik 6109	Plastik 6271
Viscosity	cPs	3500-4000	100 – 200	250 – 300
Solids	%	15 – 19	6 – 10	18 – 21
Density	g/cm^3	0.82 – 0.88	0.83 – 0.89	0.85 – 0.91
Drying time	min.	10 – 15	60	5 – 20
Reactivation temperate	^0C	70	-	-

2.2 Experimental Techniques

2.2.1 Surface Treatments

For the application of the surface treatment one must take into account the materials which are intended to be bonded. This work took into account the following points:

- Variables for the surface treatment of leather

a. The leather substrates were subjected to a mechanical treatment;
b. The primer (Plastik 6271) was applied and allowed to dry for 5 to 20 minutes at room temperature;

- Variables for the surface treatment of PU

a. The PU substrates were subjected to a mechanical treatment;
b. The primer (Plastik 6109) was applied and allowed to dry about 1 hour at room temperature;

- Procedure for the manufacture of single lap joint

a. The adhesive, Plastik 6275, was applied in both substrates and allowed to dry for 10 to 15 minutes at room temperature;
b. The adhesive films were activated by Infrared (IR) radiation at about 70° C for 6 seconds;

c. The substrates, were bonded in the desired position, as seen in Figure 3;
d. The adhesive joint was subjected to 2 to 4 bar of pressure for 4 to 5 seconds.

For the mechanical treatment, a P24 aluminium oxide abrasive cloth was used.

The adhesive joints, after being pressed, were stored in standard conditions (23º C, 50% relative humidity, Hr) during 24h, in order to ensure the complete cure of the adhesive. Only then they were subjected to the peel test.

2.2.2 Fourier Transform Infrared Spectroscopy (FTIR)

The IR spectra of the treated samples were obtained using a PerkinElmer Spectrum Two (Llantrisant, UK).

The attenuated total multiple reflection technique (ATR) was used to analyse the chemical modifications produced in about 5 µm depth on the materials surface.

The sample was directly placed on the diamond ATR top plate mounted in the sample beam of the spectrometer. The measurements were completed within 30 seconds and the ATR spectrum was obtained. Two hundred scans were obtained and averaged with a resolution of 4 cm^{-1}. The incident angle of the IR radiation was 45°.

2.2.3 Scanning Electron Microscopy (SEM)

Scanning electron microscope (SEM) analyses were produced in a JEOL JSM 6301F/ Oxford INCA Energy 350/Gatan Alto 2500 microscope (Tokyo, Japan). This equipment was used to analyse the external surface modifications on the

PU and on the natural leather produced by the treatments. The samples were secured on copper mounts by means of a silver paste and were gold-coated before the SEM micrographs were obtained.

2.2.4 Contact Angle Measurements

Contact angle measurements were carried out using the sessile drop method. Diodomethane was chosen as the test liquid. Measurements were obtained at 25°C. Single drops of diodomethane were placed on the surface of the PU and leather untreated and treated, and the contact angle for all surfaces was measured. Although the values obtained for PU were always reproducible, at least three measurements on the same sample were obtained with an error less than +/- 3 degrees. With the leather it wasn't reproducible. The leather absorbs the diodomethane too quickly, not allowing the reading of the contact angle.

2.2.5 Peel test

In this work, for the manufacture of the joint, it was decided not to study the full sole and upper combination, but instead smaller peel specimens were manufactured.

The adhesive joint studied is composed of two substrates (150mm x 30mm) glued together in an area of 100mm x 30mm, as shown in Figure 2.

Figure 2 – Test piece geometry

In the production of the adhesive joints, taking into account the material under study, the surface treatments were considered as variables, in order to be able to identify their importance in the peel strength. Therefore, the first step was making an application of all treatments commonly used in the footwear industry, followed by the manufacture of an adhesive joint without any surface treatment. In addition, joints were fabricated where only one of the treatments was performed. Other combinations were done in order to examine the effect of treatments. For the preparation of this work, for leather/PU joints, the test plan identified in Table 4 was followed.

Table 4 - Test plan for specimens leather/PU

Mat.	Surface treatment	Tests combinations					
		1	2	3	4	5	6
PU	Mechanical	X		X		X	X
	Primer	X			X	X	X
Leather	Mechanical	X	X	X	X	X	
	Primer	X	X	X	X		X

24 hours after the manufacture of the adhesive joint, the peel test was performed in the testing machine at a speed of 50 mm/min. The results are expressed as load (N) versus displacement (mm). The peel strength per unit of width was determined by the ratio between the maximum force and the width of the overlap joint. Three adhesive joint specimens for each test were considered.

The tensile machine used was an Instron (Norwood, MA, USA), model 3367, with load cell of 30kN.

3. RESULTS

The following sections list the test results and their discussion, the chemical and physical characterization of materials with and without treatment as well as the behaviour of joints when subjected to peel tests.

3.1 Chemical characterization of the materials surfaces

Figure 3 shows the spectrum obtained for the PU surface without any surface treatment.

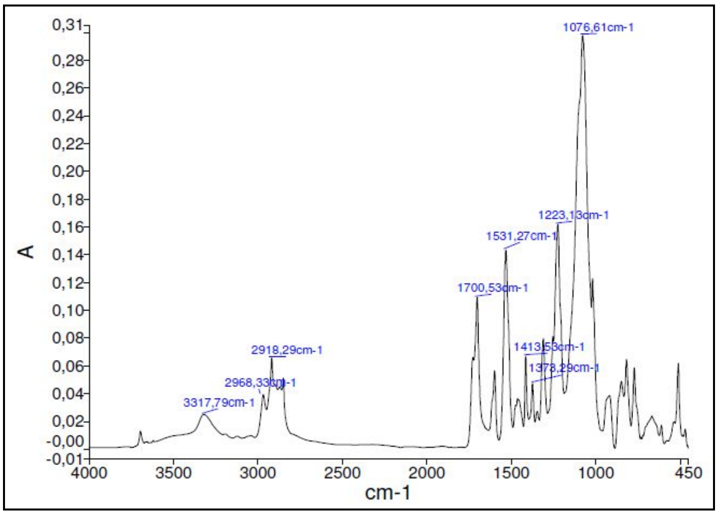


Figure 3 - ATR-IR spectrum of the PU untreated

Analysing the spectrum above we can verify the presence of absorption bands related to PU. The absorption bands corresponding to each of the above compounds are listed below (Table 5):

Table 5 – Functional groups and absorption bands of PU untreated

Functional group	Absorption bands (cm^{-1})
N-H bending (hard segment)	3317.79; 1531.27
C-H stretching (soft segments)	2968.33; 2918.29; 1413.53; 1373.29
C=O stretching (hard segment)	1700.53
C-O-O stretching (hard segment)	1223.13; 1076.61

Figures 4 and 5 present the main chemical changes on the PU surface resulting from the mechanical treatment and primer, respectively.

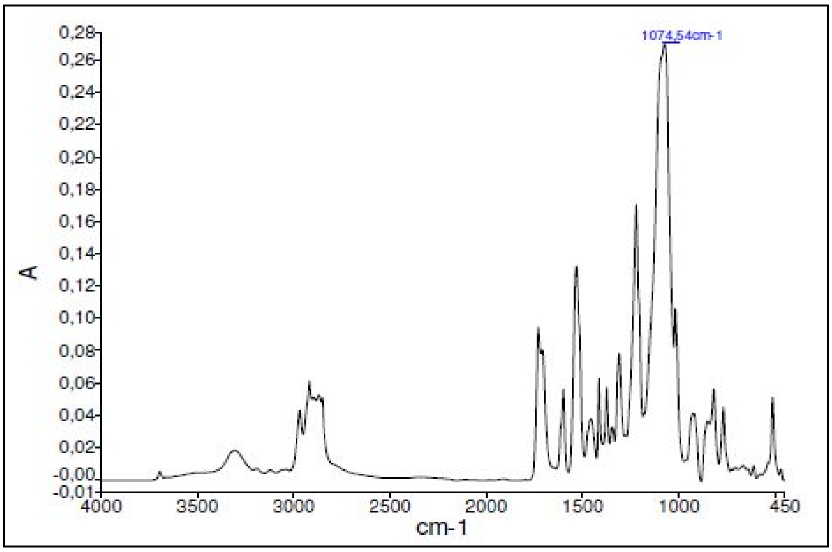


Figure 4 - ATR-IR spectrum of PU with mechanical treatment.

Figure 4 shows that with mechanical treatment of the PU, changes can be observed. Decrease of characteristic absorption bands on 1076.61 cm^{-1}, corresponding to the functional group Si-O-Si.

Figure 5 shows the ATR-IR spectrum obtained for the PU surface, after mechanical treatment and application of primer. The ATR-IR spectrum represented in Figure 6 shows the chemical modifications by primer (Plastik 6109) in the PU surface.

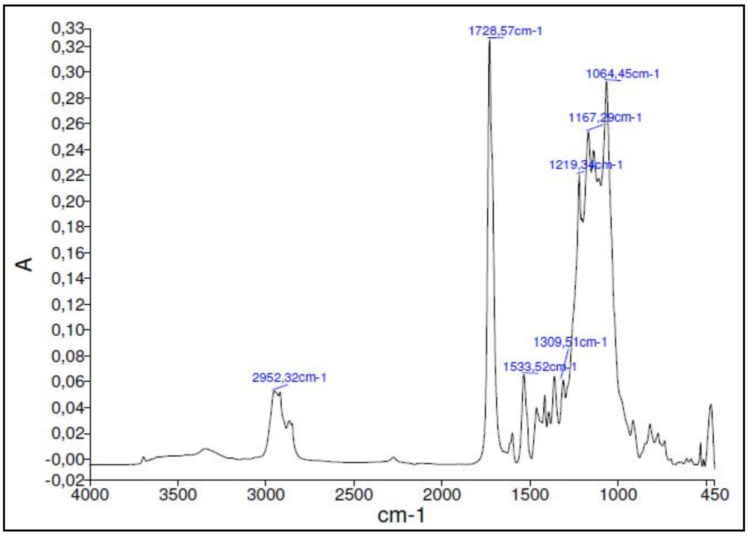


Figure 5 - ATR-IR spectrum of the PU with surface treatment (mechanical treatment and primer)

Figure 5 shows that the application of primer on PU surface, produces a coating effect. Such modifications can be evidenced by the appearance of new absorption bands compared to those present on the surfaces of untreated PU. Analysing the spectrum above we can verify the presence of absorption bands related to the primer film. The absorption bands corresponding to each of the above compounds are listed below (Table 6):

Table 6 – Functional groups and absorption bands of PU with surface treatment (primer)

Functional group	Absorption bands (cm^{-1})
C-H stretching	2952.32
C=O stretching	1728.57
N-H bending N-C=O symmetric stretching	1533.52
C-N stretching	1309.55
C-O stretching	bands at 1100 – 1240
N-H out-of-plane deformation	bands at 700

The ATR-IR analysis of the surface of the natural leather without treatment (Figure 6) indicates that it presents essentially the absorption bands related to the polypeptide chains of collagen: NH stretching (3297.75 cm^{-1}), CH_2 and CH_3 stretching (2917.59, 2849.48 cm^{-1}), C = O stretching (1647.43 cm^{-1}), N-H stretching (1462.13 cm^{-1}), C-N stretching (1237.26 cm^{-1}), C-O stretching (1035.52 cm^{-1}). Figure 6 refers to the main absorption bands for untreated natural leather.

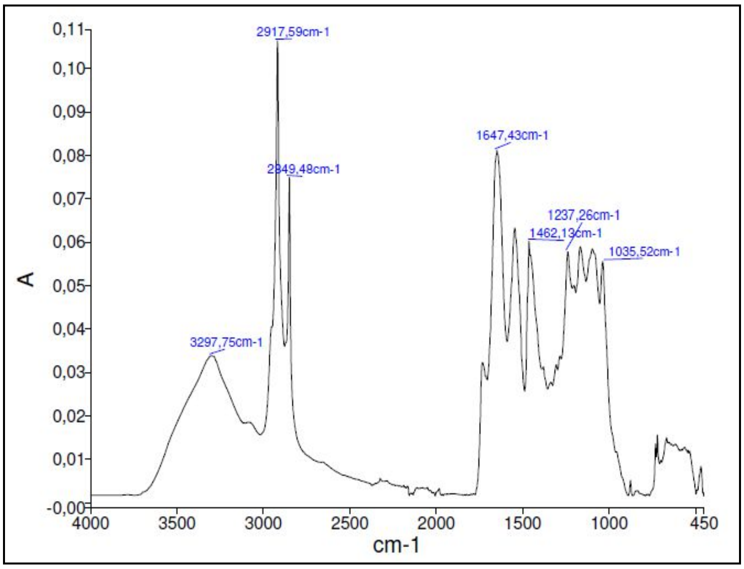


Figure 6 - ATR-IR spectrum of natural leather untreated

Table 7 shows the assignment of the most relevant absorption bands for untreated natural leather.

Table 7 – Functional groups and absorption bands of natural leather

Functional group	Absorption bands (cm^{-1})
O-H stretching	3000 – 3500
N-H stretching	3297.75
-CH_2, CH_3 stretching	2917.59, 2849.48
C=O stretching	1647.43
N-C=O stretching	1544.11
CH_2, CH_3 stretching	1462.13
C-N stretching	1237.26
C-O stretching	1035.52

For bonding the PU to natural leather, an adhesive based on polyurethane (Plastik 6275) was applied. In this case the application of mechanical (carding) and a primer treatment on the leather surface is required. The primer applied on the leather (Plastik 6271), has the same chemical nature of the adhesive and will regulate the penetration of the adhesive into the substrate, whereas the leather is extremely porous, promoting in this way the chemical compatibility between the substrate and adhesive.

Figures 7 and 8 present the main chemical changes on the leather surface resulting from the mechanical treatment and primer, respectively.

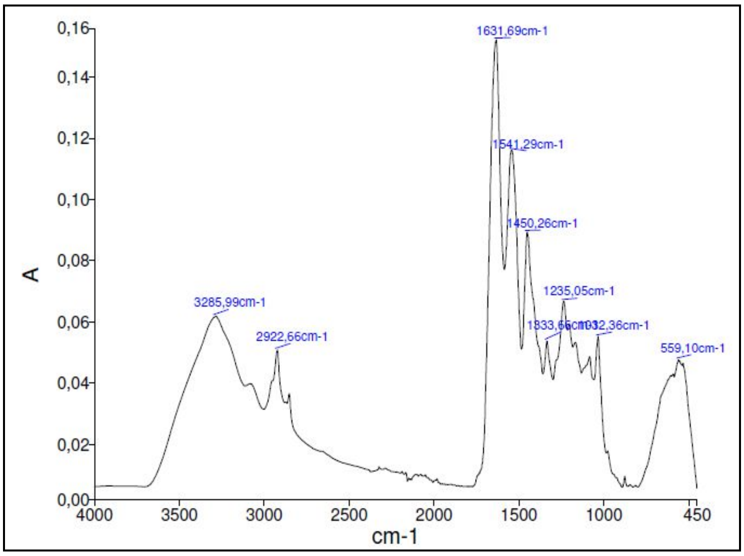


Figure 7 - ATR-IR spectrum of natural leather with mechanical treatment.

Figure 7 shows that with mechanical treatment of the natural leather, changes can be observed. The decrease of characteristic absorption bands, C-H stretching (2917.59, 2849.48 cm^{-1}), and, on the other hand, the increase of the intensity of the bands due to C = O stretching (1647.43 cm^{-1}) and N-H stretching (1544.11 cm^{-1}).

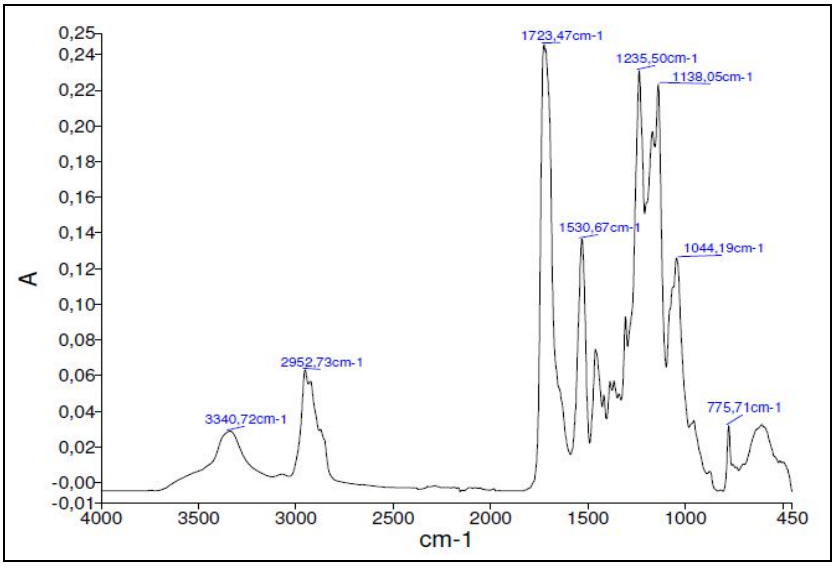


Figure 8 - ATR-IR spectrum of natural leather with mechanical treatment and primer.

Analysing Figure 8, the absorption bands correspond to the primer. Table 8 shows the most relevant absorption bands of the natural leather with mechanical treatment and primer.

Table 8 – Functional groups and absorption bands of natural leather with mechanical treatment and primer

Functional group	Absorption bands (cm^{-1})
N-H stretching	3340.72
C-H stretching	2952.73
C=O stretching	1723.47
N-H bending and N-C=O symmetric stretching	1530.67
C-N stretching	1235.50
C-O stretching	bands at 1100 to 1235
N-H out-of-lane deformation	775.71

3.2 Topological characterization of the materials surfaces

Figures 9, and 10 present SEM micrographs obtained for PU substrates with and without surface treatment, increased 30x and 100x, respectively.

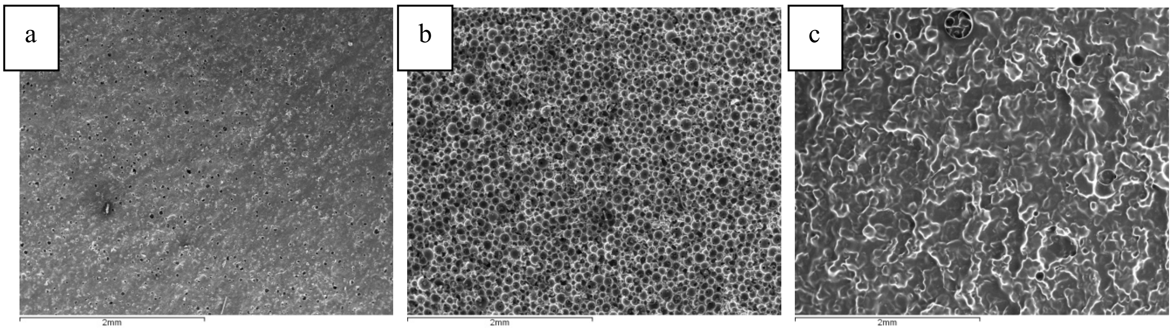


Figure 9 - SEM micrographs (30x) of PU: a) untreated, b) with mechanical treatment, c) with mechanical treatment and primer

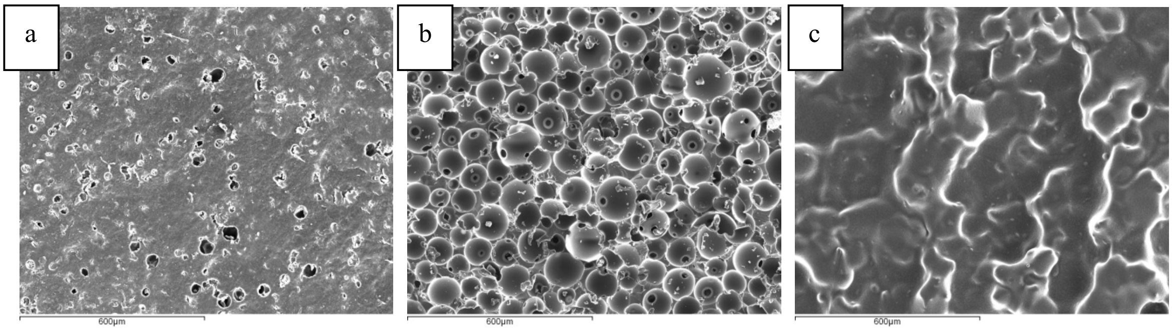


Figure 10 - SEM micrographs (100x) of PU: a) untreated, b) with mechanical treatment, c) with mechanical treatment and primer

It can be observed that the surface of PU without surface treatment showed a smooth appearance, quite different from that presented by both treatments on PU.

The mechanical treatment surface removes a layer on the PU, resulting in exposure of cavities in the surface, Figure 9-10 (b). When the primer is applied, Figure 9-10 (c), the cavities of the PU surface are covered, forming a coating.

As for PU, the morphological changes introduced on the leather surface due to application of specific surface treatment were also evaluated. Figures 11 and 12 represent the SEM micrographs obtained for leather substrates with and without surface treatments, increased 30x and 100x, respectively.

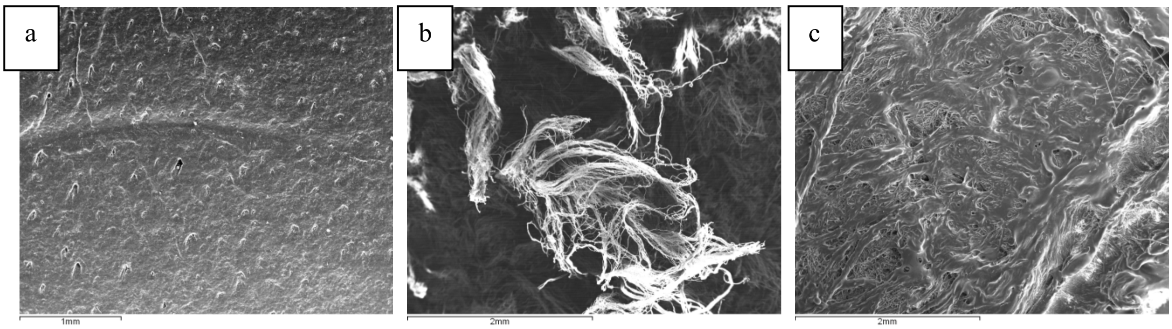


Figure 11 – SEM micrographs (30x) of natural leather: a) untreated, b) with mechanical treatment, c) with mechanical treatment and primer

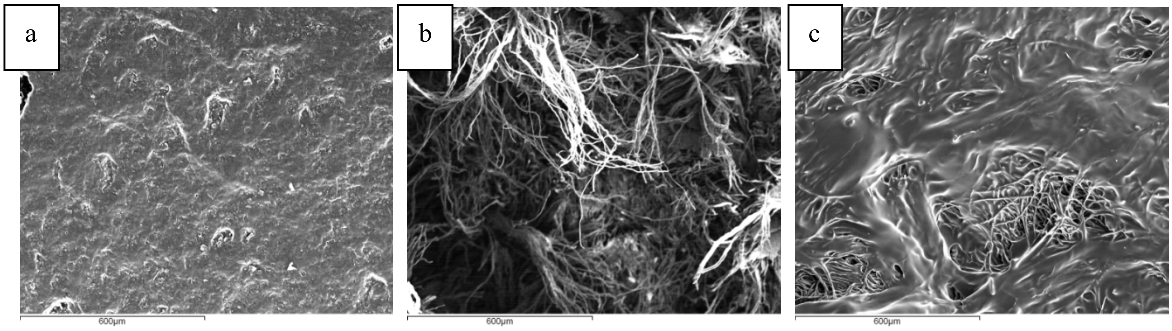


Figure 12 – SEM micrographs (100x) of natural leather: a) untreated, b) with mechanical treatment, c) with mechanical treatment and primer

As can be seen in Figures 11 and 12, the surface of the leather, after suffering surface treatment ((b) and (c)), presents a higher irregularity than that presented by untreated leather. With a magnification of 100x (Figure 12) it can also be observed that the mechanical surface treatment, caused by the removal of the weak grain layer of the leather, results in increased exposure of collagen fibres in the surface. When the primer in applied (Figure 11c, Figure 12 c), the collagen fibres become more compacted on the surface.

Regarding the differences provided by the surface due to the application of the primer Plastik 6271 (c), it may be observed from Figure 12 the appearance of a solid layer on the surface.

3.3 Contact angle characterization of the materials surfaces

The wettability of the untreated and treated PU rubber surface, was characterized by contact angle measurements. Table 9 shows the contact angle values obtained after placing drops of diodomethane on the untreated and treated PU rubber surfaces, as we can see on the Figure 13.

Table 9 – Contact angle values (diodomethane) on PU rubber surface untreated and treated

	Untreated	Treated	
PU	84.50	(1)	58.40
		(2)	22.60

(1) With mechanical treatment surface
(2) With mechanical treatment surface and primer

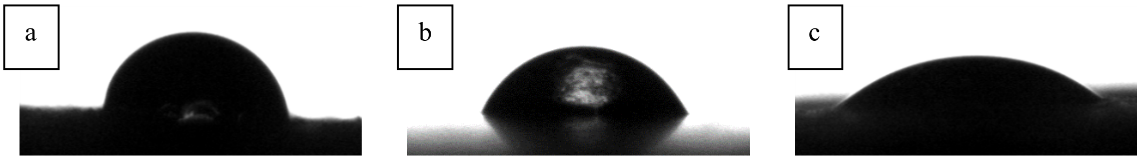
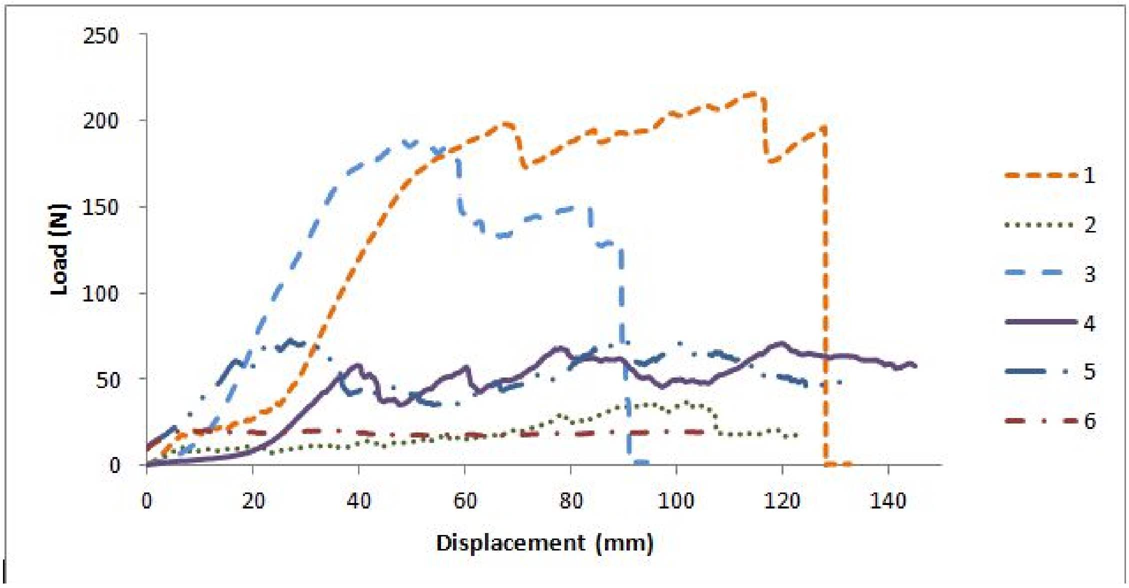


Figure 13 – Drop of diodomethane on PU surface: a) untreated, b) with mechanical treatment, c) with mechanical treatment and primer

The untreated PU rubber shows a relatively high contact angle (84.50 degrees) due to the poor wettability. Treatment produces a decrease in contact angle values on the PU rubber surface, caused by the removal of the coating produced when the sole is injected with the aid of a mold release agent.

3.4 Analyses of the peel strength of the adhesive joint

Figure 14 shows the load-displacement curves for different surface treatments of the adhesive joints using leather/PU.



1 - PU: mechanical treat., primer; Leather: mechanical treat., primer. **2 -** PU: untreated; Leather: mechanical treat., primer. **3 -** PU: mechanical treat.; Leather: mechanical treat., primer. **4 -** PU: primer; Leather: mechanical treat., primer. **5 -** PU: mechanical treat., primer; Leather: mechanical treat.. **6 -** PU: mechanical treat., primer; Leather: primer.

Figure 14 - Peel tests: leather/PU (representative shown curve for each case)

Maximum load per unit width values and standard deviation associated with each test are shown in Figure 15.

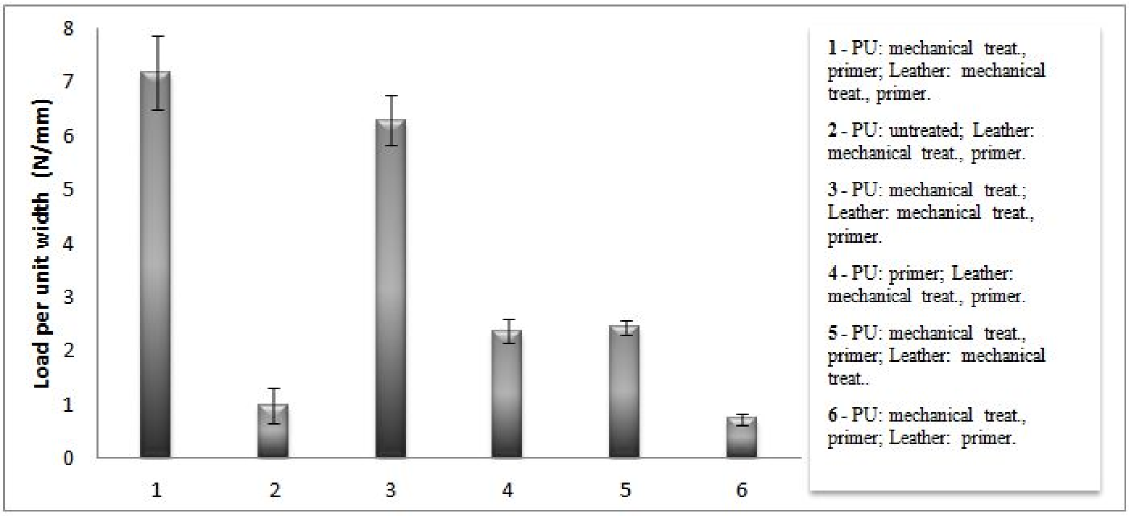


Figure 15 - Adhesive joint Leather/PU: maximum load per unit width and standard deviation

Table 10 shows the different types of failure identified on the tested joints, divided according to their treatment.

Table 10 – Adhesive joint leather/PU: types of failure of the peel tests

	PU: mechanical, primer; **Leather: mechanical, primer**	**PU: untreated;** **Leather: mechanical, primer**	**PU: mechanical;** **Leather: mechanical, primer**	**PU: primer;** **Leather: mechanical, primer**	**PU: mechanical, primer;** **Leather: mechanical**	**PU: mechanical, primer;** **Leather: primer**
Observations						
Fig.	a)	b)	c)	d)	e)	f)

Figure 14 shows that when all surface treatments are applied to PU, the joint failure is cohesive on the PU substrate, and the same was verified when mechanical treatment was applied as shown in Table 10.

When surface treatments are not applied there is adhesive joint failure, through the joint interface between adhesive and PU. The same is verified when only primer is applied as a surface treatment (see Table 10).

4. DISCUSSION

During the course of this work it was found that the simultaneous application of all surface treatments on leather/PU adhesive joint provides the highest failure strength in the peel test. Taking into account that the leather has a low surface tension, if a mechanical treatment is not applied, the application of a mechanical treatment and primer on the PU does not cause any improvement in the joint strength and joint failure occurs at the surface layer of the leather. That is, joint failure occurs by the interface adhesive / leather. If only a mechanical treatment is applied on the leather, it is possible to obtain an increase of the peel strength. The primer on the leather works as a reinforcement. The mechanical treatment allows the anchoring of the adhesive and will decrease the thickness of the leather. When primer and mechanical treatment are combined, the peel strength of an adhesive joint is increased.

The contact angle analyses confirm the influence of the surface treatment on the PU, because increase the wettability of it surface.

In the PU, if only the mechanical treatment is applied, the peel values obtained are high. However, the same cannot be said if only the primer is applied on PU. Table 11 shows values of the peel strength per unit width of the joint leather/PU.

Table 11 - Adhesive joint leather/PU: peel strength per unit width

Surface treatments	Maximum load (N)	Peel strength per unit width (N/mm)
PU: mechanical treat., primer; Leather: mechanical treat., primer	215	7.17
PU: untreated; Leather: mechanical treat., primer	29	0.96
PU: mechanical treat.; Leather: mechanical treat., primer	188	6.28
PU: primer; Leather: mechanical treat., primer	71	2.36
PU: mechanical treat., primer; Leather: mechanical treat.	73	2.43
PU: mechanical treat., primer; Leather: primer	22	0.72

Comparing the values of Table 11 and the minimum values defined by the standard EN 20344, as shown in Table 1, it was found that to obtain conform results of bonding, for baby shoes it is necessary to apply on the leather the mechanical treatment and on PU the primer or mechanical treatment. In the men, women and children footwear, it is necessary to apply a mechanical treatment and primer on the leather, and on PU the mechanical treatment must be applied, with the maximum strength being obtained when the primer is also applied.
In this work, the spectrum FTIR allowed us to detect functional groups present on the material surfaces. Comparing the untreated surface of the materials with the application of the mechanical treatment, we can verify the removal of some substances present on the PU and on the leather surface. On the PU, after the removal the mould release agent used during its injection, it’s possible to detect a decrease on the Si-O-Si band. On the leather, removal of the outer layer promotes the exposure of collagen fibres ("corium") according to the changes observed on the bands.
Analysing the spectrum of the both materials (Figure 5 and 8) treated with primer we can conclude that essentially we can see the bands corresponding to the primer.

The surface treatments on PU decrease the contact angle, which is consistent with the expectations, taking into account the results obtained with the strength obtained with the peel test of the adhesive joint: leather / adhesive / PU.

5. CONCLUSIONS

The information obtained in this work allows determining the influence of surface treatments for the manufacture of leather/PU adhesive joints. It can be concluded that to maximize peel strength of the leather/PU joints it is necessary to apply as surface treatment:

- on PU - mechanical treatment and primer.
- on leather - mechanical treatment and primer,

However, considering the most demanding footwear, adhesive joints already meet the requirements defined by EN 20344 with the application of surface treatments:

- on PU - mechanical treatment.
- on leather - mechanical treatment,

These conclusions allow manufacturers of footwear to minimize the number of operations in the manufacture of shoes, while still being capable of satisfying the minimum requirements for the sector.

In this work, the peel strength of the adhesive joint were monitored after 72 hours, however, PU adhesives are known for their high durability. The durability of the PU adhesive is compromised when the adhesive joint is subjected to high temperatures, when the footwear is subject to improper condition for which it was designed or when the joint is not properly manufactured.

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CIPADE, LINOS and Flexsol materials required for the manufacture of adhesive joints.

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PAPER 5

SINGLE OBJECTIVE OPTIMIZATION: PEEL STRENGTH

SENSITIVITY AND OPTIMIZATION OF PEEL STRENGTH BASED ON COMPOSITION OF ADHESIVES FOR FOOTWEAR INDUSTRY

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ABSTRACT

In order to contribute to the research and development of adhesives for the footwear industry, this paper aims to develop a model capable to predict and optimize the peel strength from the composition of adhesives. The proposed approach is based on three stages: experimental planning of measurements, global sensitivity analysis for uncertainty propagation and optimisation procedure. The design variables are the weight percentages of the solid raw material constituents such as polyurethane, resins and additives of the adhesive joint.

Considering the experimental results obtained for Taguchi design points as input/output patterns, an Artificial Neural Network (ANN) is developed based on supervised evolutionary learning. Using the developed ANN a global sensitivity analysis procedure is implemented and the variability of the structural response of adhesive joint is studied.

The optimal solution for adhesives composition for maximum peel strength is investigated based on ANN model and using a Genetic Algorithm. The proposed approach is able to predict the optimal peel strength including its sensitivity to uncertainties. The results show that the sensitivities of design variables belonging to polyurethane and additive groups are important for optimal adhesive joint. The optimal peel strength based on proposed approach is consistent with the experimental testing data.

Key-words: Peel strength, footwear adhesive joints, Artificial Neural Network, global sensitivity analysis, optimization, genetic algorithm.

1. INTRODUCTION

The footwear industry is increasingly characterized by quality, comfort and beauty of its models. Hence, there has been an increase in exports, evident over the past years. While comfort is determined by the selection of materials and the shoe design, quality is determined by the construction of the shoe, being also a reflection of the materials used and the manufacturing process of the adhesive joint [1]. For the manufacture of the adhesive joint, one must take into account the need for an adhesive capable of promoting adhesion required by the selected materials [2, 3]. The selection of optimum adhesive for the adhesive joint is not always an easy task because the materials differ and, in many cases, the materials selected for construction of a model shoe are subjected to surface treatments, which increases the complexity of the manufacturing process but provides a better union of the materials. For the manufacture of footwear it is necessary to take into account the following operating procedures: cutting, sewing, fitting and finishing [4]. For the preparation of this work the most demanding adhesive joint was considered. The joint described in this paper is made along the fitting procedure, which adjusts the upper to the form of the shoe and proceeds to glue it to the sole [4-6].

The mechanical property considered important in the manufacture of shoes is the peel strength [7]. Therefore, it is intend to develop a model capable to predict and optimize the peel strength from the composition of adhesives. Nouranian et al. [8] investigated the effects of formulation and processing factors on the adhesion between polyurethane (PU) and plasticized poly(vinyl chloride) (pPVC) layers. The approach was developed using the Taguchi method for experimental design. The effect of the various factors on the adhesion was found and ranked. This study reveals that four main factors influencing the adhesion strength between PU and pPVC layers are PU type, PVC fusion temperature, PVC type and plasticizer content. A review of recent state of the art in optimization of properties of adhesive joints for footwear applications shows that the research in this area is just beginning.

2. PROBLEM DEFINITION

In this work, the considered materials are natural leather for the upper and thermoplastic rubber (TR) for the sole. Physical and chemical surface treatments are applied such as mechanical carding and halogenations, respectively. The adhesive formulation is composed of a number of substances which gives the final adhesive certain mechanical properties, depending on the substrates that are part of the adhesive joint. The aim of this work is to develop a model where the design variables are the individual substances that compose the formulation of the adhesives and the results from the peel strength of this adhesive joint. Therefore, the design variables are the solid raw material constituents such as polyurethanes (PUs), resins (REs) and additives (ADs). The adhesive joint performance is measured by peel strength.

The proposed approach is based on three stages: experimental planning of measurements, global sensitivity analysis for uncertainty propagation and optimization procedure. Considering the experimental results obtained for Taguchi design points as input/output patterns, an Artificial Neural Network is developed based on supervised evolutionary learning [9-11]. After, using the developed ANN a Monte Carlo simulation procedure is implemented and the variability of the structural response of adhesive joint based on global sensitivity analysis is studied [9-11].

An approach based on the optimal design of adhesive composition to achieve the target of maximum peel strength under constraints is proposed. During the optimization process the solutions are evaluated using the optimal ANN previously obtained.

3. EXPERIMENTAL TESTS

3.1 Materials

The TR material considered in this work is TTSC TR-2531-80C. The properties of this material were provided by the manufacturer of the sole (technical datasheet of the material) and are presented in Table 1. The Halinov 2190 [12] was used as halogenate for TR. The Plastik 6271 [12] was selected as a primer for the leather.

Table 1. Physical properties of the TTSC TR-2531-80C.

Physical properties	Method	units	Sonaflex TTSC-2531-80C
Density	ASTM D792	g/cm^3	0.92 – 0.98
Hardness	DIN 53505	Shore A	77 – 83
Tensile	DIN 53504	MPa	≥ 4
Elongation at rupture	DIN 53504	%	≥ 300
Abrasion resistance	DIN 53516	mm^3	≤ 250
Flexion resistance	BS 5131:2.1 (150000 cycles)	mm/Kc	< 0.1

3.2 Experimental techniques

This work focuses on the peel strength, which is intended to evaluate the mechanical behaviour of the PU adhesive solvent-based when bonding leather to TR soles, while taking into account the composition of adhesives. The peel strength is a property which determines the strength required to peel of two materials, where at least one of the substrates is flexible. This test enables to distinguish if an adhesive is fragile or ductile [5, 13].

To quantify this property the peel test was performed in a tensile testing machine, which is a standard test [14]. Two standards are used for footwear industry adhesives: ISO 20344:2004 (shoe) [15], EN 1392:1998 (specimen) [16]. ISO 20344:2004 is designed to evaluate the bonding properties of soles where adhesion is measured by determining whether or not it is acceptable for the desired effect. This standard allows obtaining the peel strength per unit width, which is the average load per unit width, applied at an angle between 90° and 180°, depending on the flexibility of the substrate, in relation to the joint, needed to lead to rupture. In the footwear industry, independently of the type of materials used, to ensure its durability, it is necessary for adhesive joints fulfilling certain specifications defined by EN 20344, which establishes the minimum values to consider for difficult bonding.

For the application of the surface treatment one must take into account the materials which are intended to be bonded. This work took into account the following points:

- Parameters for the surface treatment of leather: (1) the leather substrates were subjected to a mechanical treatment; (2) the primer was applied and allowed to dry for 5 to 20 minutes at room temperature;

- Parameters for TR surface treatment: (3) the TR substrate was subjected to chemical treatment and allowed to dry at least 1 hour at room temperature;

- Procedure for the manufacture of single lap joint: (4) the adhesive was applied in both substrates and allowed to dry for 10 to 15 minutes at room temperature; (5) the adhesive films were activated by Infrared (IR) radiation at about 70 °C for 6 seconds; (6) the substrates were bonded in the desired position, as seen in Figure 1; (7) the adhesive joint was subjected to 2 to 4 bar of pressure for 4 to 5 seconds.

For the mechanical treatment, a P24 aluminium oxide abrasive cloth was used. The adhesive joints, after being pressed, were stored in standard conditions (23 ºC, 50% Hr) during 72h, in order to ensure the complete cure of the adhesive. Only then they were subjected to the peel test.

In this work the full sole is not considered to build the testing joint. Instead smaller peel specimens were manufactured. The adhesive joint studied is composed of two substrates (150mm x 30mm) glued together in an area of 100mm x 30mm, as shown in Figure 1.

The first step was making an application of all treatments commonly used in the footwear industry, followed by the manufacture of an adhesive joint with experimental tests. The experimental portion of this work consisted of the analysis of peel strength in the single lap joint, subjected to tensile loading as shown in Figure 2 according to the procedures defined in EN 1392:1998.

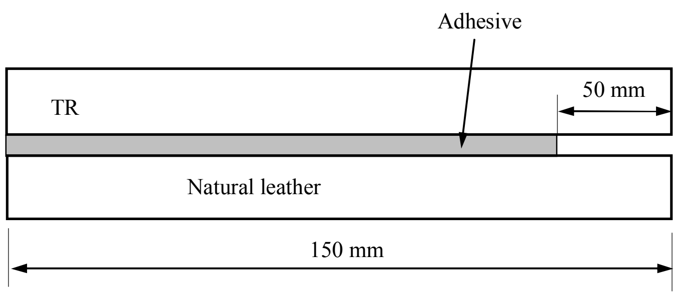

Figure 1. Test piece geometry.

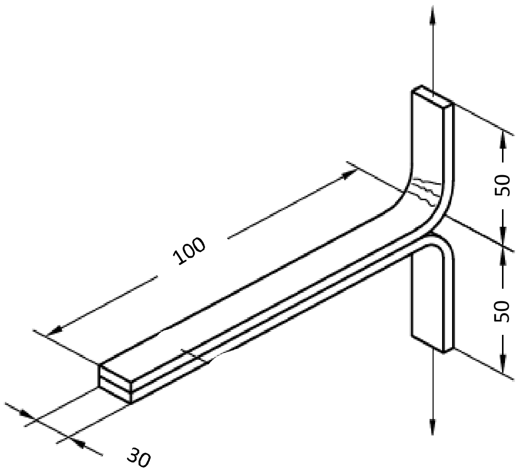

Figure 2. Adhesive joint for peel test (dimensions mm).

One day after the manufacture of the adhesive joint, the peel test was performed in the testing machine at a speed of 50 mm/min. The results are expressed as load (N) versus displacement (mm). The peel strength per unit of width was determined by the ratio between the maximum force and the width of the overlap joint. Three adhesive joint specimens for each test were considered. The tensile machine used was an Instron (Norwood, MA, USA), model 3367, with load cell of 30kN.

3.3 Planning of experimental measurements

In this work the Taguchi method [17] was used to plan the experimental tests. The Taguchi method involves reducing the variation in a process through robust design of experiments.

The effect of many different parameters on the performance characteristic in a set of experiments can be analyzed by using orthogonal arrays. Once the parameters affecting a process to be measured have been determined, the levels at which these parameters should be varied must be determined. In this work, the design of experiments are implemented using the Taguchi table L27(3^{13}) [17].

4. SENSITIVITY ANALYSIS

4.1 Global sensitivity analysis (GSA)

The study of the influence of variability in input variables such as raw material compositions on the structural response of adhesive joint is an important issue. It can be implemented using local measures of sensitivity or a fully evaluation denoted Global Sensitivity Analysis (GSA). The GSA techniques are supported by variance-based methods [11], [18-20] and are adopted in this work. The objective of the proposed approach is to study the propagation of uncertainties in input variables, such as raw materials used on PU adhesives solvent based. The peel strength *PS*, is considered as the measure of structural response of the adhesive joint. On other words, the objective is to measure and to rank the importance of the variability of input variables on the structural response of adhesive joint.

Assuming that the variables are independent, the variance of the conditional expectation $var(E\langle PS|x_i\rangle)$ can be used as an indicator of the importance of the input variable x_i on the variance of *PS*. This indicator is directly proportional to the importance of x_i. In particular in this work the first-order sensitivity index of Sobol [11], [18-20] is used as normalized indicator:

$$S_i = \frac{var(E\langle PS \mid x_i\rangle)}{var(PS)} \quad (1)$$

One difficulty when using global sensitivity indices is the computational cost. In this work the Monte Carlo simulations method is used together Artificial Neural Network (ANN) aiming to estimate the Sobol indices [11, 20]. The proposed approach uses the previously planned and obtained experimental input/output pattern results into the learning procedure of the ANN. Thus, is possible to avoid the exhaustive and costly experimental tests to obtain the variability of the input variables structural on response.

4.2 ANN developments

The Artificial Neural Network (ANN) methodology is based on a computational structure inspired by the biology of the human neural system, including attributes such as learning, thinking, memorizing, remembering, rationalizing and problem solving. The ANN is made up of simple and highly interconnected nodes called neurons. One artificial neuron can modify its behavior in response to the environment where it is located. The ANNs are robust models having properties of universal approximation, parallel distributed processing, learning, adaptive behaviour and can be applied to multivariate systems [21].

The proposed ANN is organized into three layers of nodes (neurons): input, hidden and output layers. The linkages between input and hidden nodes and between hidden and output nodes are denoted by synapses. These are weighted connections that establish the relationship between input data and output data. In the developed ANN, the input data vector $\mathbf{D}^{inp}$ is defined by a set of values for design/input variables $\mathbf{x}$, which are the raw materials of the adhesives, such as PU's, resins and additives. In this approach, each set of values for the input variable vector $\mathbf{x}$ is selected using the Taguchi method [17]. The corresponding output data vector $\mathbf{D}^{out}$ contains the peel strength.

Each pattern, consisting of an input and output vector, needs to be normalized to avoid numerical error propagation during the ANN learning process. This is obtained using the following data normalization:

$$\underline{D}_k = (D_k - D_{min}) - \frac{D_N^{max} - D_N^{min}}{D_{max} - D_{min}} + D_N^{min} \tag{2}$$

where D_k is the real value of the variable before normalization, D_{min} and D_{max} are the minimum and maximum values of D_k, respectively, in the input/output data set to be normalized. According to Equation (2), the data set is normalized to values $\underline{D}_k$, verifying the conditions

$$D_N^{min} \leq \underline{D}_k \leq D_N^{max} \tag{3}$$

Depending on the input or output data, different maximum and minimum normalized values can be used in Equation (3) (0.01 and 0.99, respectively, are the most common values). The sum of the modified signals (total activation) is performed through the Activation Function. Thus, the activation of the *kth* node of the hidden layer (p=1) and output layer (p=2) is obtained through sigmoid functions as follows:

$$A_k^{(p)} = \frac{1}{1 + e^{-\eta^{(p)} C_k^{(p)}}} \tag{4}$$

where *p* represents the activation layer (either hidden or output layer) and $C_k{}^{(p)}$ are the components of the vector $\mathbf{C}^{(p)}$ given by

$$\mathbf{C}^{(p)} = \mathbf{M}^{(p)} \mathbf{D}^{(p)} + \mathbf{r}^{(p)} \tag{5}$$

where $\mathbf{M}^{(p)}$ is the matrix of the weights of synapses associated with the connections between input and hidden layers (*p*=1) or between hidden and output layers (*p*=2), $\mathbf{r}^{(p)}$ is the biases vector on the hidden (*p*=1) or output (*p*=2) layers, $\mathbf{D}^{(p)}$ is the input data vector for the hidden (*p*=1) or output (*p*=2) layer.

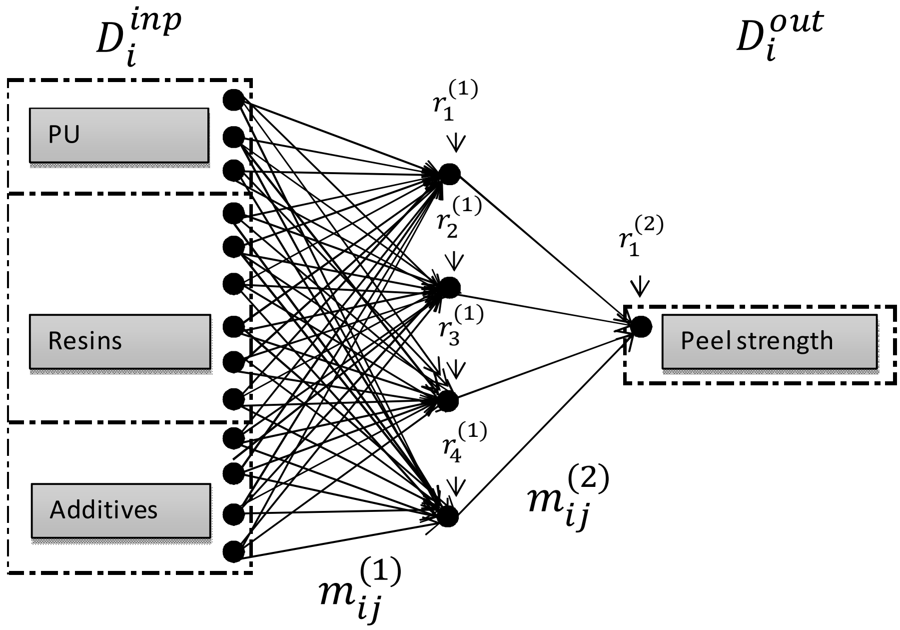

Figure 3. Artificial Neural Network topology.

The scaling parameters $\eta^{(p)}$ influence the sensitivity of the sigmoid activation functions and must be controlled. The weights of the synapses, $m_{ij}^{(p)}$, and biases in the neurons at the hidden and output layers, $r_k^{(p)}$, are controlled during the learning process. Figure 3 shows the topology of the ANN, showing the input and output parameters.

The error between predefined output data and ANN simulated results is used to supervise the learning process, which is aimed at obtaining a complete model of the process. As a set of input data are introduced to the ANN, it adapts the weights of the synapses and values of the biases to produce consistent simulated results through a process known as learning. For each set of input data and any configuration of the weight matrix $\mathbf{M}^{(p)}$ and biases $\mathbf{r}^{(p)}$, a set of output results is obtained. These simulated output results are compared with the predefined values to evaluate the difference (error), which is then minimized during the learning procedure. The root-mean-squared error is considered as

$$RMSE = \sqrt{\frac{1}{N_{exp}} \sum_{i=1}^{N_{exp}} \left(PS_i^{sim} - PS_i^{exp} \right)^2} \tag{6}$$

where N_{exp} is the number of experiments considered in the set of design points of Taguchi and the superscripts *sim* and *exp* denote the simulated and experimental data of Peel strength, *PS*. To reinforce the error minimization the following relative error component is also considered:

$$RE = \frac{1}{N_{exp}} \sum_{i=1}^{N_{exp}} \left| \frac{PS_i^{sim} - PS_i^{exp}}{PS_i^{exp}} \right| \tag{7}$$

The influence of the biases of the neurons of the hidden and output layers is also included to stabilize the learning process:

$$\Gamma = \sqrt{\frac{1}{N_{exp}} \sum_{i=1}^{N_{exp}} \left[\frac{1}{N_{hid}} \sum_{k=1}^{N_{hid}} \left(r_k^{(1)} \right)^2 \right]} + \sqrt{\frac{\left(r_1^{(2)} \right)^2}{N_{exp}}} \tag{8}$$

The errors obtained from Equations (6) to (8) are reflected in the ANN learning procedure using the following formula:

$$F_1\left(\mathbf{M}^{(p)}, \mathbf{r}^{(p)}\right) = c_1\, RMSE + c_2\, RE + c_3\, \Gamma \tag{9}$$

This means that the weights of the synapses and biases can be modified until the errors fall within a prescribed value. Therefore, the weight of the synapses in matrix $\mathbf{M}^{(p)}$, and biases of the neurons of the hidden and output layers in vector $\mathbf{r}^{(p)}$, are modified to reduce the differences (supervised learning) throughout the learning process.

The adopted supervised learning process of the ANN is based on a Genetic Algorithm (GA) [22-24] using the weights of synapses $\mathbf{M}^{(p)}$, and biases of neural nodes at the hidden and output layers $\mathbf{r}^{(p)}$, as design variables. A binary code format is used for these variables. The number of digits of each variable can be different depending on the connection between the input-hidden layers or hidden-output layers. The bounds of the domain of the learning variables and scaling parameters $\eta^{(p)}$, are the control parameters. The optimization problem formulation associated with the ANN learning process is based on the minimization of the errors defined in Equation (9) without constraints. So, the fitness function to be minimized in GA search to obtain the optimal ANN configuration is

$$FIT^{(1)} = F_1\left(\mathbf{M}^{(p)}, \mathbf{r}^{(p)}\right) \tag{10}$$

A GA is an optimization technique based on the survival of the fittest and natural selection theory proposed by Charles Darwin. The GA basically performs on three parts: (1) coding and decoding design variables into strings; (2) evaluating the fitness of each solution string; and (3) applying genetic operators to generate the next generation of solution strings in a new population. Four basic genetic operators, namely selection, crossover, Elimination/Replacement and mutation are used in this paper. An elitist strategy based on conservation of the best-fit group transfers the best-fitted solution into a new population for the next generation.

The operators are applied in the following sequence:

- Step1: Initialization. Random generation of the initial population.
- Step 2: Selection. Population ranking according to solution fitness. Definition of the elite group including highly-fitted individuals. Selection of the progenitors, p_1 and p_2: one from the best-fitted group (elite) and another from the least fitted one. This selection is done with a probability depending on the merit of each individual/solution. Transferring of the whole population S^{k} to an intermediate step where they will join the offspring group **B** determined by the Crossover operator.
- Step 3: Crossover. The crossover operator transforms two chromosomes (progenitors) into a new chromosome (offspring) having genes from both progenitors. The offspring genetic material is obtained using the *parameterized uniform crossover* [22, 23]. This is a multi-point

combination technique applied to the binary string of two selected chromosomes p_1 and p_2. This Crossover is applied with a predefined probability to select the offspring genetic material from the highest fitted chromosome. The offspring group **B** created by Crossover will be joined to the original population S^k generating the enlarged population $S^k \cup \mathbf{B}$.

- Step 4: Elimination/Replacement. The enlarged population of solutions $S^k \cup \mathbf{B}$ is ranked according to their fitness. Then, it follows Elimination of solutions with similar genetic properties and subsequent replacement by new randomly generated individuals. The new enlarged population is ranked and the individuals with low fitness are excluded. Now, the dimension of the current population is less than the original one. The original size population will be recovered after including a group of new solutions obtained from the Mutation operator.
- Step 5: Mutation. The Mutation genetic operator is used to overcome the problem induced by Selection and Crossover operators where some generated solutions have a large percentage of equal genetic material. To avoid the rising of local minima a set of randomly generated chromosomes is introduced into the population. This operation is called *Implicit Mutation* and is quite different from classic techniques where a reduced number of genes are changed. Indeed, this group of chromosomes will be recombined with the remaining individuals into the population during next generations. The Mutation operator guarantees the diversity of the population in each generation. After mutation, the new population S^{k+1} is obtained and the evolutionary process will continue until the stopping criteria are reached.
- Step 6: Stopping criterion. The stopping criterion used in the convergence analysis is based on the relative variation of the mean fitness of a reference group during a fixed number of generations and the feasibility of the corresponding solutions. The search is stopped if the mean fitness of the reference group does not evolve after a finite number of generations. Otherwise, the population evolves to the next generation returning to Step 2.

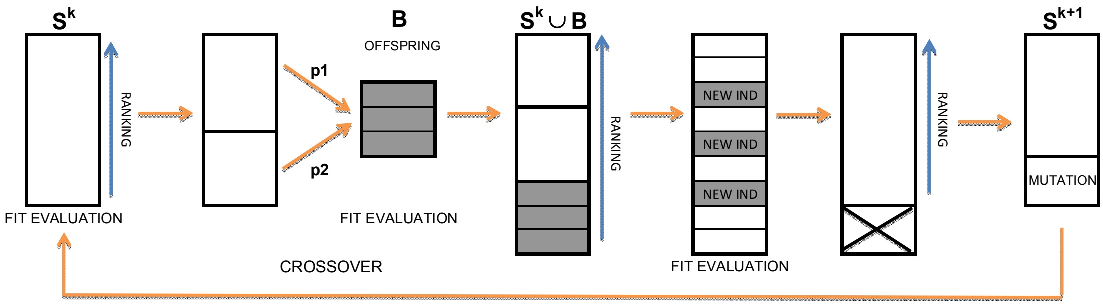

Figure 4. Steps of GA at each generation.

Figure 4 shows the flow diagram of the implemented genetic algorithm. Further details on creating and using a GA for ANN learning can be found in references [22-24]. At the end of the learning procedure the optimal configuration of ANN, denoted by $\mathbf{X}_{\mathrm{ANN}}{}^{\mathrm{opt}}$, is obtained.

4.3 GSA based on ANN-Monte Carlo approach

The variability influence of each input design variable on peel strength is based on ANN-Monte Carlo approach aiming to estimate of GSA indices. To reduce the computational costs the analysis is implemented considering only the Sobol first-order sensitivity index defined in Equation (1). The methodology to obtain the conditional variances and the system variance is based on the algorithm proposed by António and Hofbauer [11, 20] as follows:

- 1st Step: Lets consider the non-correlated input parameters vector **x** following a uniform probability distribution function $Unif(0,1)$.
- 2nd Step: Considers a set of random numbers λ_{fix} following a uniform probability distribution function $Unif(0,1)$. These N_f random numbers are used to generate the fixed values of the input parameter x_i.

- 3rd Step: For each input parameter x_i (not for itself) a sample matrix $\mathbf{J}_\alpha$ is generated by independently collecting samples of (*p*-1) random numbers following a uniform distribution $Unif(0,1)$, where the size of the sample is N_r.
- 4th Step: For each input parameter x_i a combination of values of $\boldsymbol{\lambda}_{fix}$ and $\mathbf{J}_\alpha$ is defined. The structural response of *PS* is evaluated for **x** using the optimal ANN. After, the conditional expectation of structural response is estimated and the mean values of this conditional expectation are calculated. Finally, the variance of the conditional expectation of structural fixing each input parameter x_i is estimated. The procedure is repeated for all input parameters.
- 5th Step: The variance of structural response $var(PS)$, is estimated considering the previous simulations.
- 6th Step: Calculation of the global Sobol sensitivity index using Equation (1) for all input parameters.

5. OPTIMIZATION OF ADHESIVE JOINT

5.1 Optimization problem definition

The structural response of adhesive joint is measured by peel strength *PS*, which represents the objective function of the problem. The design variables denoted by vector **x** with components x_k, are the weight percentages of PUs, resins and additives in the adhesive composition. The mathematical formulation of the optimization problem of adhesive joint is defined as peel strength maximization subject to technological constraints as follows,

$$Maximize\ \ PS(\mathbf{x})\ ,\ \ \text{over}\ \ \mathbf{x}\ , \tag{11}$$

subject to:

$$10 \le \sum_{k=1}^{p} x_k \le 20 \tag{12}$$

$$\sum_{k=1}^{r} x_{p+k} \le 1 \tag{13}$$

$$\sum_{k=1}^{a} x_{r+k} \le 7 \tag{14}$$

$$x_k^l \le x_k \le x_k^u \quad , \quad k = 1, \cdots, p + r + a \tag{15}$$

where *p*, *r* and *a* are the number of materials of each group of PUs, resins and additives considered for the adhesive joint, respectively. The constants x_k^l and x_k^u are the lower and upper bounds of design variable x_k, respectively.

5.2 Optimal design procedure

The proposed optimization algorithm is based on two stages as shown in Figure 5. In the first stage using the Taguchi design points the ANN-based on GA is developed. In this stage the GSA is implemented using the optimal configuration of ANN denoted by $\mathbf{X}_{\mathrm{ANN}}{}^{\mathrm{opt}}$. During the second stage the peel strength, *PS* is maximized under the constraints defined from Equation (12) to Equation (15). The fitness evaluation is based on optimal configuration $\mathbf{X}_{\mathrm{ANN}}{}^{\mathrm{opt}}$ of the ANN obtained at the first stage.

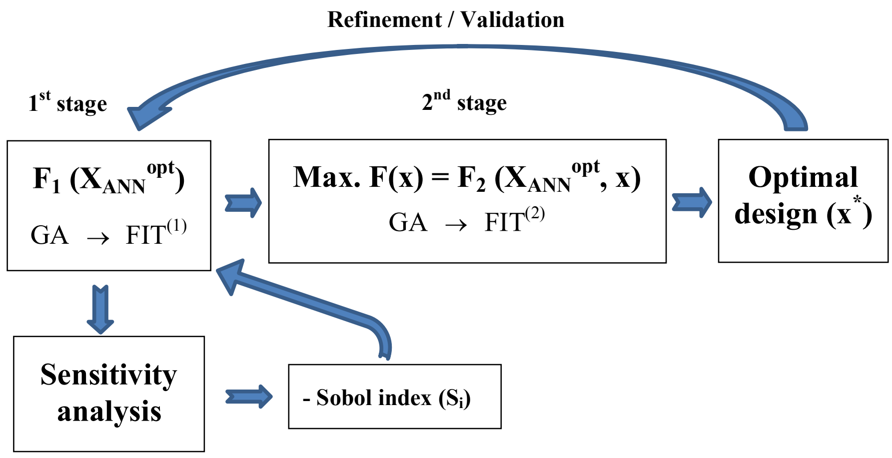

Figure 5. Flow diagram of optimization procedure.

The optimization procedure continues aiming the refinement and validation of the optimal solution. The refinement of the design space and the uncertainty propagation control can be obtained from the sensitivity analysis.

The evolutionary search is based on a population of solutions. Each solution is ranked according its value. So, it is necessary to define the fitness, which is related with the objective function and the constraints of the problem defined from equation (11) to equation (15). During the last few years several methods were proposed for handling constraints by genetic algorithms. In this work the adopted method is based on graded penalization of the individuals/solutions according to its constraint violation [22, 23]. The genetic algorithms will seek to increase the fitness as it operates. So, the original optimization problem from equation (11) to equation (15) is transformed as follows:

$$\mathit{Maximize} \quad FIT^{(2)} = \alpha_1 \, PS(\mathbf{x}) - \alpha_2 \sum_{i=1}^{N_g} \Phi_i(\mathbf{x}) \tag{16}$$

with $$\Phi_i(\mathbf{x}) = \begin{cases} 0 & , \quad \text{if} \;\; \varphi_i(\mathbf{x}) \le 0 \\ K_i \left| \varphi_i(\mathbf{x}) \right|^{q_i} & , \quad \text{if} \;\; \varphi_i(\mathbf{x}) > 0 \end{cases} \tag{17}$$

where $\varphi_i(\mathbf{x})$ are the constraints defined from equation (12) to equation (14) and normalized by their bound limits. Here, $\varphi_i(\mathbf{x}) \leq 0$ are associated to the feasibility of the constraint $\varphi_i(\mathbf{x})$. The N_g constraints defined from Equation (12) to Equation (14) must be normalized relatively to their bound limits aiming to avoid scaling effects. The size constraints in Equation (15) are imposed directly to the design space at the binary code format transformation.

From equation (16) and (17) it can be established that designs with good fitness and satisfying the constraints have priority in the rank process. Solutions of the problem that violate the constraints are penalized at a graded degree of severity according to the difference between the actual and the allowable values. The constants q_i and K_i are evaluated considering two constraint violation degrees, i.e., strong penalization for large violation value and fair penalization for negligible violation of the constraints [22, 23]. The constants α_i must be large enough to avoid negative fitness.

The evolutionary search aiming to solve the constrained maximization problem formulated in equations (16) and (17) is based on the same GA presented in section 4.2. However, in this case the fitness function of the constrained problem is $FIT^{(2)}$ that depends on design variable vector **x** associated with the raw material constituents used in the adhesive formulation. The genetic parameters for the GA used in this second stage are selected in independent way relatively to the first stage of the proposed approach.

6. RESULTS AND DISCUSSION

6.1 Experimental results

To test the proposed approach to adhesive formulations, a several compositions are considered, as shown in Table 2.

Table 2. Materials used in adhesive joint and Taguchi levels definition.

Materials		% weight on formula	Leve ls	Real value
PU's:				
1.	**Caprolactone with extremely high crystallization**	0-20	1/2/3	2.5/5/10
2.	**Polyester with extremely high crystallization**	0-20	1/2/3	2.5/5/10
3.	**Polyester with very high cryistallization**	0-20	1/2/3	2.5/5/10
Resins:				
4.	**Colophony WW**	0-1	1/2/3	0/0.2/0.5
5.	**Hydrocarbon (C9)**	0-1	1/2/3	0/0.2/0.5
6.	**Alkyl phenolic**	0-1	1/2/3	0/0.2/0.5
7.	**Terpene phenolic**	0-1	1/2/3	0/0.2/0.5
8.	**Coumarone-Indene**	0-1	1/2/3	0/0.2/0.5
9.	**Vinyl Chloride / Acetate Vinyl**	0-1	1/2/3	0/0.2/0.5
Additives:				
10.	**Fumaric Acid**	0-0.6	1/2/3	0/0.3/0.6
11.	**Hydrophobic silica**	0-2	1/2/3	0/1/2
12.	**Nitrocellulose**	0-2	1/2/3	0/1/2
13.	**Chlorinated rubber**	0-3	1/2/3	0/1.5/3
Constraints:				
Total % PU		10-20		
Total % Resins		0-1		
Total % Additives		0-7		

The Taguchi design points used to plan the experiments are considered as input values in the ANN learning procedure. A number of 27 training data sets are selected inside the interval domain of each design (random) variable and levels defined in Table 2.

The Taguchi values are selected according to the approach proposed by Taguchi and Konishi [17]. By the selected Taguchi table L27(3^{13}) the actual composition for each Taguchi design point is obtained, as shown in Table 3. The values presented in Table 3 and Table 4 are used as input/output patterns for learning procedure of ANN.

Table 3. Taguchi design points: % weight on formulation (design variables values).

Design point	Material number												
	1	2	3	4	5	6	7	8	9	10	11	12	13
1	2.5	2.5	2.5	0	0	0	0	0	0	0	0	0	0
2	2.5	2.5	2.5	0	0.2	0.2	0.2	0.2	0.2	0.3	1	1	1.5
3	2.5	2.5	2.5	0	0.5	0.5	0.5	0.5	0.5	0.6	2	2	3
4	2.5	5	5	0.2	0	0	0	0.2	0.2	0.3	2	2	3
5	2.5	5	5	0.2	0.2	0.2	0.2	0.5	0.5	0.6	0	0	0
6	2.5	5	5	0.2	0.5	0.5	0.5	0	0	0	1	1	1.5
7	2.5	10	10	0.5	0	0	0	0.5	0.5	0.6	1	1	1.5
8	2.5	10	10	0.5	0.2	0.2	0.2	0	0	0	2	2	3
9	2.5	10	10	0.5	0.5	0.5	0.5	0.2	0.2	0.3	0	0	0
10	5	2.5	5	0.5	0	0.2	0.5	0	0.2	0.6	0	1	3
11	5	2.5	5	0.5	0.2	0.5	0	0.2	0.5	0	1	2	0
12	5	2.5	5	0.5	0.5	0	0.2	0.5	0	0.3	2	0	1.5
13	5	5	10	0	0	0.2	0.5	0.2	0.5	0	2	0	1.5
14	5	5	10	0	0.2	0.5	0	0.5	0	0.3	0	1	3
15	5	5	10	0	0.5	0	0.2	0	0.2	0.6	1	2	0
16	5	10	2.5	0.2	0	0.2	0.5	0.5	0	0.3	1	2	0
17	5	10	2.5	0.2	0.2	0.5	0	0	0.2	0.6	2	0	1.5
18	5	10	2.5	0.2	0.5	0	0.2	0.2	0.5	0	0	1	3
19	10	2.5	10	0.2	0	0.5	0.2	0	0.5	0.3	0	2	1.5
20	10	2.5	10	0.2	0.2	0	0.5	0.2	0	0.6	1	0	3
21	10	2.5	10	0.2	0.5	0.2	0	0.5	0.2	0	2	1	0
22	10	5	2.5	0.5	0	0.5	0.2	0.2	0	0.6	2	1	0
23	10	5	2.5	0.5	0.2	0	0.5	0.5	0.2	0	0	2	1.5
24	10	5	2.5	0.5	0.5	0.2	0	0	0.5	0.3	1	0	3
25	10	10	5	0	0	0.5	0.2	0.5	0.2	0	1	0	3
26	10	10	5	0	0.2	0	0.5	0	0.5	0.3	2	1	0
27	10	10	5	0	0.5	0.2	0	0.2	0	0.6	1	2	1.5

Table 4. Peel strength [N/mm] for Taguchi design points obtained by experiments.

Design point	Peel strength	Design point	Peel strength	Design point	Peel strength
1	4.13	**10**	5.51	**19**	7.91
2	2.36	**11**	7.41	**20**	7.41
3	0.28	**12**	2.31	**21**	7.86
4	8.92	**13**	7.60	**22**	7.77
5	5.24	**14**	3.88	**23**	5.48
6	4.79	**15**	7.59	**24**	7.72
7	7.44	**16**	7.18	**25**	4.78
8	8.28	**17**	7.66	**26**	6.56
9	7.96	**18**	7.13	**27**	7.12

On an initial analysis, when confronted Tables 3 and 4, we can see that maximizing the amount of resins and additives and minimizing the amount of polyurethane on the adhesive formulation, we obtain very low peel strength. These features show the needs to implement an optimization procedure.

6.2 ANN learning for optimal configuration

A number of 4 neurons are considered for the hidden layer of the ANN topology described in section 4.2. The ANN learning process is formulated as an optimization problem based on minimization of fitness $FIT^{(1)}$ defined in equation (10). The ANN-based GA learning process is performed using a population of 21 individuals in evolutionary search. The elite and mutation groups have seven and four solutions, respectively [22]. The binary code format with five digits is adopted for weights of synapses and biases of neural nodes at both input-hidden and hidden-output linkages. The learning process is concluded after 30000 generations. The constants in Equation (9) are $c_1 = 10$, $c_2 = 0.1$ and $c_3 = 0.1$.

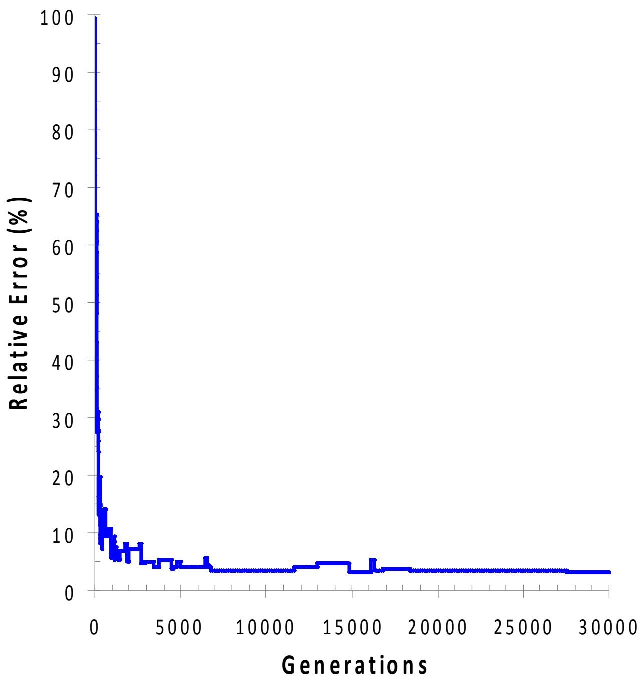

Figure 6. Evolution of mean relative error at ANN-based GA learning process.

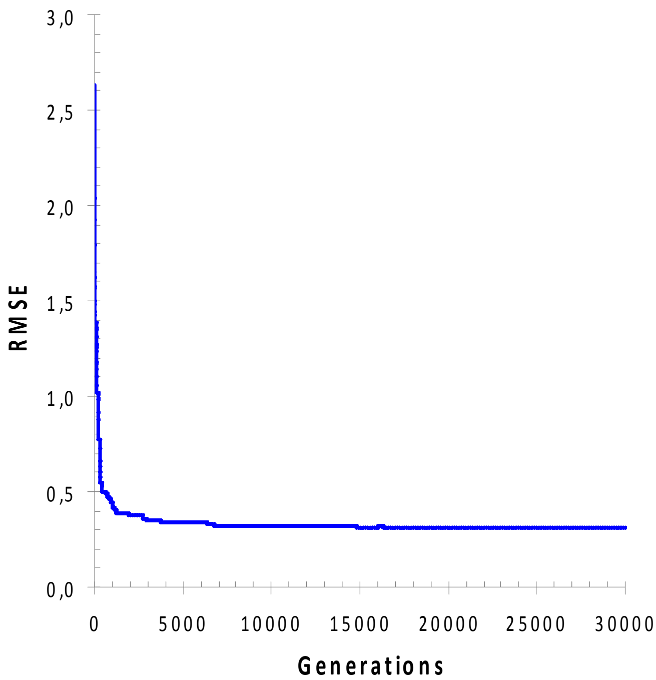

Figure 7. Evolution of root-mean squared error at ANN-based GA learning process.

Figures 6 and 7 show the evolution of the error parcels at ANN-based GA learning process. Those error components was defined in Equation (6) an Equation (7). The relative error of 3.2% is reached for optimal configuration $\mathbf{X}_{\mathrm{ANN}}{}^{\mathrm{opt}}$ of the developed ANN.

6.3 GSA results

Figure 8 shows the importance measure of the design variables. These design variables are the solid raw material constituents such as polyurethanes, resins and additives, and are identified in Table 2. The GSA indices are obtained through ANN-Monte Carlo approach based on the algorithm proposed in Section 4.3. In this algorithm the values $N_f = 50$ and $N_r = 100$ are used to obtain the conditional probability for Sobol index.

The histograms of results presented in Figure 8 are obtained from Equation (1) in section 4.1. They represent the contribution (%) of the variance of the conditional expectation, $var(E\langle PS|x_i\rangle)$, for the total variance of peel strength, *var*(*PS*). Both variances are obtained considering the sampling procedures associated with ANN-Monte Carlo simulation algorithm. One first-order Sobol index per design variable x_i is obtained using the equation (1).

The performance of the adhesive joint is very sensitive to the influence of polyurethanes (materials 1, 2 and 3). A particular sensitivity to polyesters is observed. The sensitivity of the performance to the resins Coumarone-Indene (material 8) and Vinyl Chloride / Acetate Vinyl (material 9) is also important. Although the contribution of the additives is related with the improvement of mechanical behaviour of PUs and resins, their influence on peel strength is shown through the sensitivities of Hydrophobic silica (material 11) and Chlorinated rubber (material 13).

The GSA results in Figure 8 can help the designer to decide on the most important design variables to be considered for the optimization in second stage of the procedure.

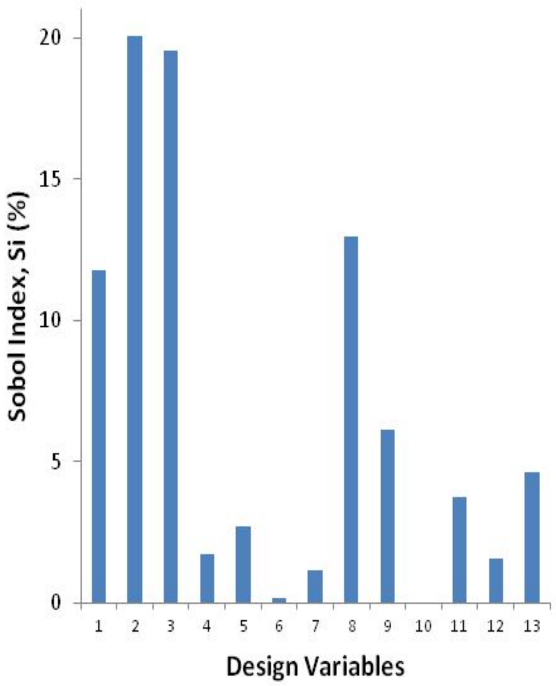

Figure 8. Importance measure of the input design variables by first-order Sobol index.

6.4 Optimization results and discussion

The optimization procedure during the second stage corresponds to constrained maximization of peel strength, *PS* as defined from Equation (11) to Equation (15). The fitness function $FIT^{(2)}$, depends on design variable vector **x** associated with the raw material constituents used in the adhesive formulation. The fitness evaluation is based on optimal configuration $\mathbf{X}_{\mathrm{ANN}}{}^{\mathrm{opt}}$ of the ANN obtained at the first stage.

From the previous GSA it is possible to decide on the most important variables for the optimization of the second stage procedure. However, it is intended with this analysis to compare both results, obtained from the sensitivity analysis and from the optimization process, from the qualitative point of view. Thus, all design variables will be considered for the second stage.

The constraints in Equation (12) to Equation (14) are normalized as previously referred in Section 5.2. The constants q_i and K_i in constraint term on Equation (16) and Equation (17) are calculated considering two constraint violation degrees, as follows:

- a penalization equal to 500 for strong violation value equal to 0.005
- a penalization equal to 100 for fair violation value equal to 0.001

The constants $\alpha_1 = \alpha_2 = 1.$ are considered in Equation (16) for this application.

The constrained evolutionary search is performed using a population of 21 individuals. The elite and mutation groups have seven and four solutions, respectively [22]. The binary code format with four digits is adopted. A number of 5000 generations was considered in evolutionary search applied to second optimisation stage. Figure 9 shows the behaviour of peel strength, *PS*, during the constrained maximization procedure. An improvement of 22% relatively to the best initial value was reached and the corresponding optimal solution is shown in Figure 10.

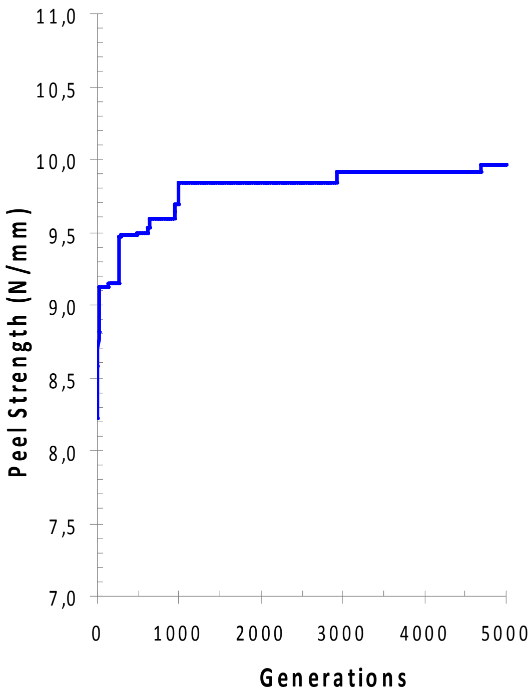

Figure 9. Evolution of peel strength constrained maximization during GA search.

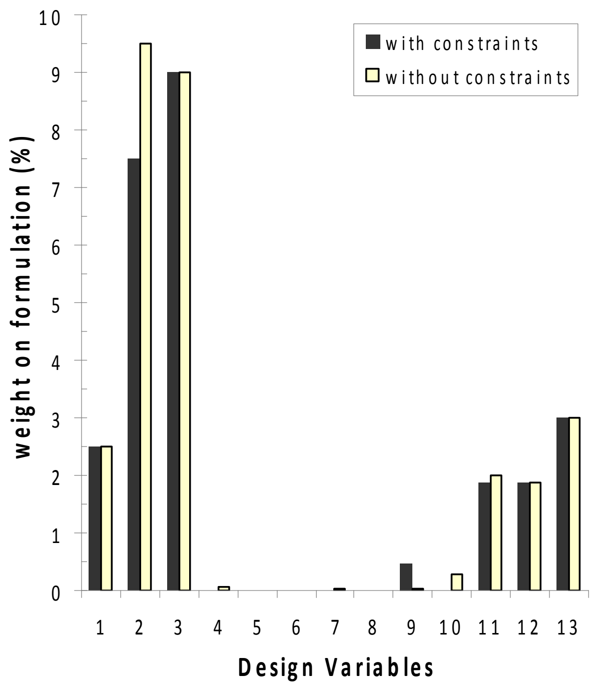

Figure 10. Optimal solutions for adhesive formulation.

A second optimization problem of peel strength maximization is solved without imposition of technological constraints defined from equation (12) to equation (14) (only with size constraints in equation (15)). Figure 10 shows a comparison of solutions for raw material constituents of adhesive joint with and without consideration of the referred constraints in the optimization problem. The optimal fitness values are equal for both cases. However, the optimal solution obtained without consideration of referred technological constraints show the following sum values:

Total % PUs=21 %; total % Resins=0.133%; total % Additives=7.147%.

Clearly above values reveals that the total percentages of PUs and Additives do not satisfy the bound limits of the original optimization problem. Indeed, the inclusion of the constraint term in the fitness function $FIT^{(2)}$ is important.

The same calculations for the solution with inclusion of technological constraints defined from equation (12) to equation (14) gives,

Total % PUs=19 %; total % Resins=0.466%; total % Additives=6.733%,

That is fallen inside the constraint intervals presented in Table 2.

Finally, from comparison analysis of Figure 8 and Figure 10 it can be concluded that the sensitivities of the design variables belonging to the resins' group are not important for the optimization process. On contrary, the sensitivities of the other groups are important.

The optimal result obtained for peel strength based on proposed approach is consistent with the experimental testing data used to implement the model. Indeed, the peel strength is maximized when large quantities for PUs and for additives are considered, as shown in Table 3 and Table 4 for Taguchi design points 4 and 8.

The use of the ANN obtained at the first stage of the proposed approach enables to simulate all regions of the design space at the second stage of the procedure. On contrary, by the planning of experiments based on Taguchi technique, only discrete points can be considered. So, comparing the results of Figure 10 (optimization) with the ones in Table 4 (experimental), it is possible to conclude that the peel strength values from optimization process are higher than the ones obtained from experimental tests.

Although the experimental tests are necessary to quantify the real properties of adhesive joints, the proposed two-stage ANN-GA optimization approach shows improved explorative properties of the design space. Furthermore, the GSA at the first stage combined with the ANN-GA optimization process at second stage, can be a powerfully tool to obtain the refinement of optimal solutions for adhesive joints formulations.

7. CONCLUSIONS

A model capable to predict and optimize the peel strength of the footwear adhesive joint, based on the composition of adhesives was presented. The proposed approach is based on three stages: experimental planning of measurements, global sensitivity analysis for uncertainty propagation and optimisation procedure. The design variables are the weight percentages of the solid raw material constituents such as polyurethane, resins and additives of the adhesive joint.

A Taguchi-ANN-GA approach predicting the sensitivity of the peel strength as function of the composition of formulation used in adhesive joints was developed. The results show the robustness of the model to measure the influence of the raw material constituents on peel strength, which plays an important role on the optimal design of the adhesive joints.

The numerical results show that the sensitivities of the design variables belonging to polyurethane and additives groups are important for optimal design of the adhesive joint. The optimal results obtained for peel strength based on proposed approach is consistent with the experimental testing data used to implement the model. The proposed two-stage ANN-GA optimization approach supported by experimental tests shows improved explorative properties of design space and can be a powerfully tool for the designers of adhesive joints in footwear industry.

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PAPER 6

SINGLE OBJECTIVE OPTIMIZATION: CREEP RATE

PAPER 6

OPTIMAL DESIGN OF ADHESIVE COMPOSITION IN FOOTWEAR INDUSTRY BASED ON CREEP RATE MINIMIZATION

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ABSTRACT

On the footwear industry the composition of adhesives have a high contribute for the product quality. This paper aims to develop a model capable to predict and optimize the creep rate using the composition of the adhesive joints. The proposed mixed numerical and experimental approach is based on following stages: the planned experimental measurements; the learning procedure aiming to obtain the optimal artificial neural network (ANN) configuration; and the optimal design procedure for adhesive joint composition. The design variables are the weight percentages of the solid raw material constituents of the adhesive, such as polyurethanes (PUs), resins and additives.

Considering the experimental results obtained for Taguchi design points as input/output patterns, the ANN is developed based on supervised evolutionary learning. In the last stage the optimal solution for adhesives composition considering minimum creep rate is investigated based on ANN and genetic algorithm. The optimal results for creep rate minimization based on proposed approach are reached when large quantities for PUs and for some additives are considered, and when colophony and vinyl resin aren't considered on the formulation.

The sensitivity of the structural response of footwear adhesives to composition constituents is also studied based on Sobol indices obtained from ANN-Monte Carlo simulation procedure. The performance measured by creep rate of the adhesive joint is very sensitive to the influence of some polyurethanes and a particular sensitivity to caprolactone types with extremely high crystallization is observed. The sensitivities of the creep rate to the resins Colophony and Coumarone-Indene are also important.

Key-words: creep rate, footwear adhesive joints, Artificial Neural Network, sensitivity, optimization, genetic algorithm.

1. INTRODUCTION

In Portugal, the footwear industry has been growing significantly. This was associated to the investment in quality, comfort and design of the shoes [1]. For the quality it has been considered the selection of the raw materials aiming to manufacture the best adhesive joint, allowing accomplishing the demands of the customers [2-3].

On this industry, the polyurethane (PU) adhesives were the most used because of their range of materials applications. The PU adhesives are capable to satisfy the most demand on adhesive joints for the manufacture of the shoes [4-6].

The creep rate is one of the most important mechanical properties to be considered on the footwear industry [7]. Therefore, it is intended to develop a model capable to predict and optimize the creep rate from the raw materials used in the composition of the adhesive joint [8].

2. PROBLEM DEFINITION AND PROPOSED APPROACH

To manufacture the shoes, the considered materials are natural leather for the upper and thermoplastic rubber (TR) for the sole. It is necessary to consider surface treatment on the materials to increase the mechanicals properties, so, chemical and physical surface treatments are applied such as halogenations and mechanical carding, respectively [9-12].

The adhesive formulation is composed of a number of substances which gives to the final adhesive composition certain mechanical properties, depending on the substrates that are part of the adhesive joint [13]. The aim of this work is to develop an optimization model where the objective is the creep rate minimization and the design variables are the weight percentage of the solid raw materials that compose the formulation of the adhesives. Therefore, is considered the PU adhesives because of their excellent adhesion, so the design variables are the adhesive constituents such as polyurethanes (PUs), resins (REs) and additives (ADs) [9], [13-14]. In this work will be considered the application of the bicomponent adhesive (2K), these adhesives are composed of two components A and B [15]. Component A is the adhesive and component B is the crosslinker, in this case it is an isocyanate based. These adhesives are used when it is desired accelerate the curing of the adhesive and increase the temperature resistance of the adhesive joint. Therefore 2K adhesives are supplied separately, because when mixed the lifetime of the combination is reduced. However, it is necessary to implement the efficient mixing of the two components during the shoes manufacture, to ensure the complete reaction, providing the maximization of the mechanical properties of the adhesive [16].

In general, the outputs of the optimization model are the response results obtained for the mechanical properties of the manufactured adhesive joint. Here, the mechanical properties of the adhesive joint are measured by the creep rate. Since the creep rate parameter is associated with the performance properties for temperature resistance of adhesives it is considered as measure of the quality of the adhesive joint in footwear industry.

The first column of the proposed optimization strategy is the definition of the physical model representing the adhesive joint and the relationship between the design variables – raw materials, and the structural response – creep rate. So, the proposed approach for this first column is based on planned experimental measurements and development of the approximation model. First of all, the set of experiments are planned using the Taguchi method aiming to obtain a good representation of the physical phenomenon. Secondly, considering the experimental results obtained for Taguchi design points as input/output patterns, an Artificial Neural Network (ANN) is developed based on supervised evolutionary learning [8], [17-19].

The second column of the optimization strategy is the optimization algorithms: the first one used for ANN supervised learning and the second one used for optimal design search in creep rate constrained minimization. Both algorithms are Genetic Algorithms with independent genetic parameters.

The third column of the optimization strategy is the architecture of optimization model connecting the different modulus associated with the extraction of data necessary for optimization algorithm which comes from the optimization problem formulation. An approach based on the optimal design of adhesive composition to achieve the target of minimum creep rate under manufacturing constraints is proposed. During the optimization process the solutions are evaluated using the optimal ANN previously obtained.

Finally, inside the third column of the optimization strategy a ANN-based Monte Carlo simulation procedure is implemented aiming to study the sensitivity of the structural response of adhesive joint relatively to design variables. In particular the Sobol indices for global sensitivity analysis are used to establish the relative importance of the design variables [8], [17-19].

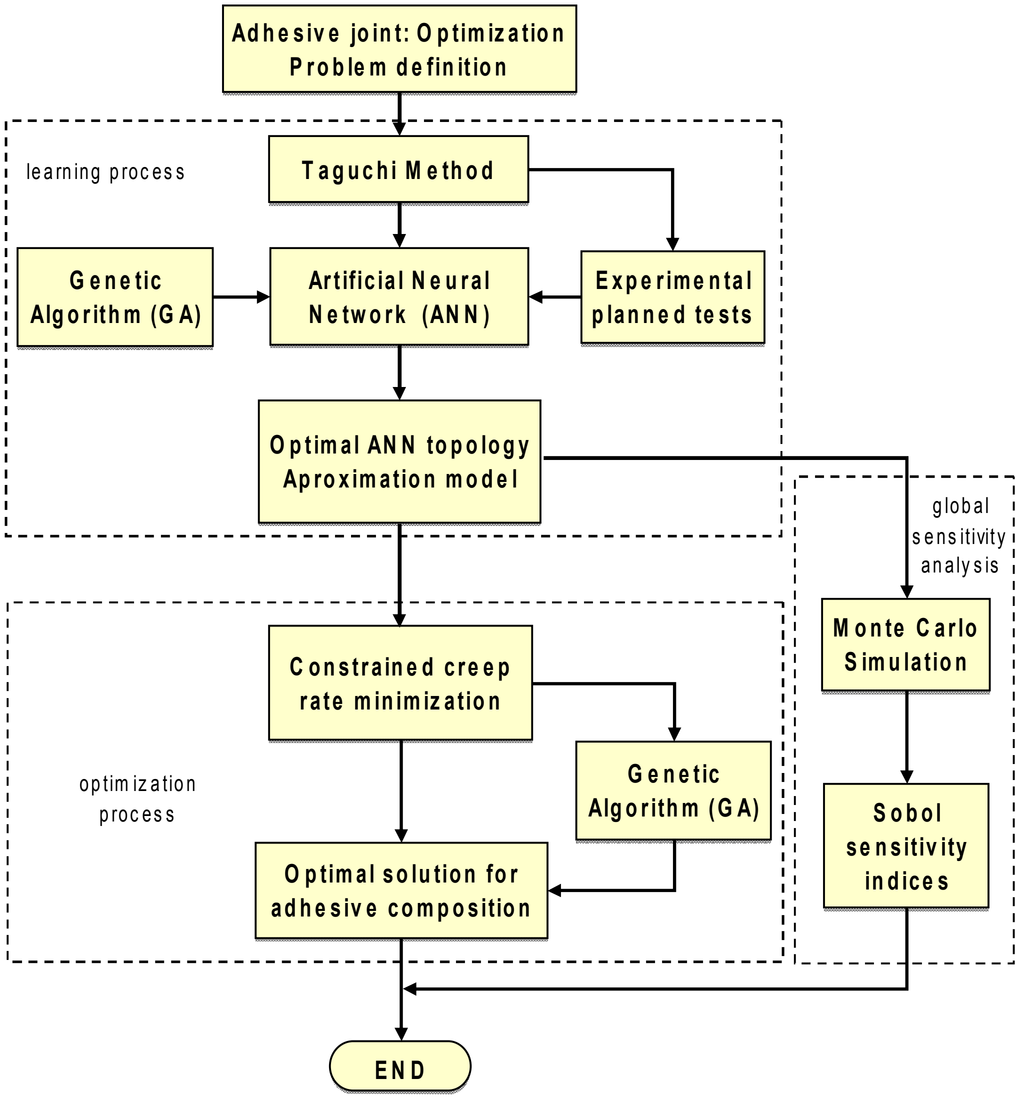

Figure 1. Flow diagram of the proposed approach.

Our definition based on Sobol indices is referred to sensitivity of the structural performance functional such as the creep rate, relatively to a specific design variable considering the joint effects of all design variables. In the proposed approach, the design variables are the weight percentages of raw materials used on the composition of the adhesive joint.

The definition of sensitivity used in this approach is based on stochastic analysis where the Sobol indices are calculated using the conditioned variance and the total system variance such as the creep rate variance of adhesive joint. Furthermore, all the variances are calculated using a Monte Carlo simulation algorithm being the creep rate values of the sample obtained by the ANN approximation model. This ANN is built after a learning procedure using the results obtained from planned experiments. So, Sobol index is an indirect measurement of the importance of each design variable on the variability of the structural response of the adhesive joint. On other words, individual Sobol index defines the contribution of the variance of the associated design variable for the total variability of the creep rate response of the adhesive joint.

Figure 1 shows the flow diagram with the different parts of the proposed approach.

3. EXPERIMENTAL TESTS

The proposed approach for the first column of the optimization strategy is based on planned experimental measurements necessary for the development of the approximation model. So, a set of experiments are implemented aiming to obtain data used in learning procedure of generation of the approximation model defining the behaviour of adhesive joint.

3.1 Materials

The TR material considered in this work is TTSC TR-2531-80C. The properties of this material were provided by the manufacturer of the sole (technical datasheet of the material) and are presented in Table 1. The Halinov 2190 [20] was used as halogenate preparation for TR. The Plastik 6271 [20] was selected as a primer for the leather, an adhesive primer usually is a diluted solution of an PU adhesive in an organic solvent [11] which depends on the nature of the substrate surface [13]. As second compound to mix on the adhesive planned by Taguchi method, it was applied Cipadur 2230T, an aromatic polyisocyanate diluted on ethyl acetate [20].

Table 1. Physical properties of the TTSC TR-2531-80C.

Physical properties	Method	units	Sonaflex TTSC-2531-80C
Density	ASTM D792	g/cm^3	0.92 – 0.98
Hardness	DIN 53505	Shore A	77 – 83
Tensile	DIN 53504	MPa	≥ 4
Elongation at rupture	DIN 53504	%	≥ 300
Abrasion resistance	DIN 53516	mm^3	≤ 250
Flexion resistance	BS 5131:2.1 (150000 cycles)	mm/Kc	< 0.1

3.2 Experimental techniques

This work focuses on the creep rate, which is intended to evaluate the mechanical behaviour of the PU adhesive solvent-based when bonding leather to TR soles, while taking into account the composition of adhesives. The creep rate is a property which determines the temperature resistance of the single lap joint [5], [16]. Creep rate is a displacement under a constant load in a constant high temperature [9]. To quantify this property the creep test was performed in a heat activator, which is a standard test [9]. The standard used for footwear industry adhesives is described on the EN 1392:1998 [21]. This standard allows obtaining the creep rate, which is the variation of displacement per unit of time [21].

For the application of the surface treatment one must take into account the materials which are intended to be bonded. On the leather is necessary to consider as surface treatment of the mechanical treatment and the application of the primer to improve a surface interaction between adhesive and the adherent [10-11]. The primer was applied and allowed to dry for 5 to 20 minutes at room temperature. For TR, it is necessary to apply a chemical treatment as a surface treatment. The TR substrate was subjected to a halogenated agent and allowed to dry at least 1 hour at room temperature. Before applying the adhesive on the single lap joint, it was mixed the second component: 95% of adhesive and 5% of Cipadur 2230T [20]. For the manufacture of single lap joint, the adhesive was applied in both substrates and allowed to dry for 10 to 15 minutes at room temperature. Then, the adhesive films were activated by Infrared (IR) radiation at about 70 °C for 6 seconds, the substrates were bonded in the desired position, as seen in Figure 2 and the adhesive joint was subjected to 2 to 4 bar of pressure for 4 to 5 seconds.

For the mechanical treatment, a P24 aluminium oxide abrasive cloth was used [10-11]. The adhesive joints, after being pressed, are stored in the following standard atmosphere conditions: 23ºC of temperature and 50% of humidity, during 72h. This is done in order to ensure the complete cure of the adhesive.

In this work the full soles are not considered to build the testing joint. Instead those, smaller creep specimens were manufactured. The adhesive joint studied is composed of two substrates (150mm x 30mm) glued together in an area of 100mm x 30mm, as shown in Figure 2.

The first step was making an application of all treatments commonly used in the footwear industry. This is followed by the manufacture of an adhesive joint using the adhesive experiments planned by the Taguchi method mixed with the second compound. The experimental portion of this work consisted of the analysis of creep rate in the single lap joint, subjected to tensile loading as shown in Figure 2 according to the procedures defined in EN 1392:1998 [21].

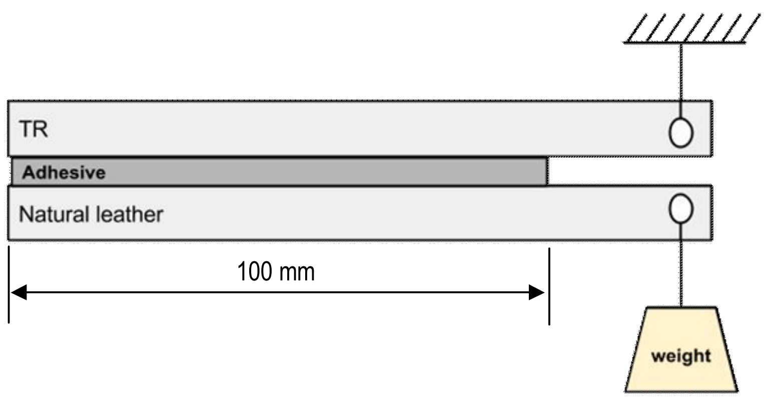

Figure 2. Test piece geometry and adhesive joint for creep test.

The creep test specimen use the same test pieces as specified in the peel test, where two strips of material up to (150 ± 2) mm long and (30 ± 0.5) mm wide are bonded to cover each other over a length of at least (100 ± 2) mm. One of the unbonded ends are fixed on the cabinet of heat activator, and the other unbonded end is loaded with a weight of 1.5 kg.

After the complete cure of the adhesive joint, the creep test was performed in the heat activator at 60ºC. The unbonded ends of the test specimen are carefully bended apart, the beginning of the bonds is marked and the ends are inserted in the clamps of the cabinet of the heat activator [21]. Then heat the test pieces in the cabinet for 1h to allow them to reach the temperature specified. After this heating up period each test specimen is loaded for 10 min with the specified constant weight (1,5 kg). Finally the cabinet of the heat activator is opened and the separations (in mm) of the bonds substrates are marked while still loaded. The time (in min) to complete separation [21] is recorded. With the creep experiment it was obtained a “creep failure envelope” that can be divided into three phases: primary, secondary and tertiary. The primary phase corresponds to an instantaneous elastic strain, the secondary phase represents the creep strength and the tertiary phase happens with the failure of the bond of the specimen [9].

Creep measurement was made by either monitoring the time and the load-dependent displacement of an adhesive joint under shear load, or simply recording the time to failure. The failure is a consequence of the cohesion decreasing at the applied temperature, defined in this work as 60^{o}C. The calculation of the mean of the separation lengths of a bond ignores the highest value -primary phase, and the lowest value - tertiary phase [21]. The creep value is determined by linear regression of the experimental results. The results are expressed as displacement (millimetres, mm) versus time (minutes, min). Three adhesive joint specimens for each test were considered. The heat activator used was a Memmert (Germany), model UM400.

3.3 Planning of experimental measurements

In this work the Taguchi method [22] was used to plan the experimental tests. The Taguchi method involves reducing the variation in a process through robust design of experiments. The effect of many different parameters on the performance characteristic in a set of experiments can be analyzed by using orthogonal arrays. Once the parameters affecting the measuring process have been determined, the levels at which these parameters should be varied must be determined. In this work, the design of experiments are implemented using the Taguchi table $L27(3^{13})$ [8], [22].

4. THE ADHESIVE COMPOSITION OPTIMIZATION

4.1 Optimization problem formulation

The proposed approach follows the problem definition established in Section 2. So, the structural response of footwear adhesive joint is measured by creep rate (*CR*), which represents the objective function of the problem to be minimized. Therefore, it is intended to develop a model capable to predict and minimize the creep rate depending on the raw materials used in the composition of the adhesive joint. These design variables denoted by vector **x** with components x_k, are the weight percentages of PUs, resins and additives in the adhesive composition. The mathematical formulation of the optimization problem of adhesive joint is defined as creep rate minimization subject to technological constraints as follows,

$$Minimize \;\; CR(\mathbf{x}) \;,\; \text{ over } \;\mathbf{x}\,, \qquad (1)$$

subject to:

$$10 \le \sum_{k=1}^{n} x_k \le 20 \qquad (2)$$

$$\sum_{k=1}^{r} x_{n+k} \leq 1 \tag{3}$$

$$\sum_{k=1}^{a} x_{r+k} \leq 7 \tag{4}$$

$$x_k^l \leq x_k \leq x_k^u \quad , \quad k = 1, \cdots, n + r + a \tag{5}$$

where *n*, *r* and *a* are the number of materials of each group of PUs, resins and additives considered for the adhesive joint, respectively. The constants x_k^l and x_k^u are the lower and upper bounds of design variable x_k, respectively.

The values of the constraints are considered, taking into account the recommendations given by polyurethane producers. According to the manufacturers should be considered valid ranges for the weight percentage values of the constituent raw materials so as to allow obtaining good results without compromising the mechanical properties of the polyurethane can give the adhesive joint. So the limits appearing in Equations (2), (3) and (4) are according to the referred suggested recommendations [20].

4.2 The proposed optimization strategy approach

The proposed approach is based on mixed experimental-numerical procedures. The experimental data obtained in previous described procedure is fundamental to perform the optimization search. Two stages are identified in numerical part of the proposed approach as shown in Figure 3. These two stages are: 1) the learning procedure aiming to obtain the optimal ANN configuration, which supports the relationship between raw materials and creep rate; and 2) the optimal design procedure based on the search for optimal adhesive joint composition. In these two stages of numerical part of the proposed approach two optimization sub-problems are solved using independent evolutionary searches such as Genetic Algorithms (GA).

In the first stage using the set of experiments for Taguchi design points the ANN approximation model is developed. The optimal configuration of ANN is obtained minimizing the error between the simulated network outputs and the experimental data for creep rate. In this stage the design variables are the weights of synapses, $m_{ij}^{(p)}$, and the biases, $r_k^{(p)}$, of the ANN as is explained in further sections. The optimization procedure is performed using the genetic algorithm denoted by $\mathbf{GA}^{(1)}$ with appropriated genetic parameters. Since the GA is a population-based evolutionary method in this stage a population of solutions for ANN configuration denoted by $\mathbf{P}^{(t)}$ is considered at each *t*-generation. After the ANN learning procedure the optimal configuration denoted by $\mathbf{P}_{\mathrm{ANN}}{}^{\mathrm{opt}}$ is obtained.

During the second stage the creep rate, C*R*, is minimized under the constraints defined from Equation (2) to Equation (5). The fitness evaluation is based on optimal configuration $\mathbf{P}_{\mathrm{ANN}}{}^{\mathrm{opt}}$ of the ANN obtained at the first stage. The optimal design procedure is performed using the genetic algorithm denoted by $\mathbf{GA}^{(2)}$ with genetic parameters different from previous stage. A population of solutions denoted by $\mathbf{X}^{(t)}$ is considered at each t-generation of this genetic search. These solutions are associated with different compositions of PUs, resins and additives for the adhesive joint. After the stopping criteria are reached, it is obtained the optimum adhesive composition. Figure 3 shows the integrated ANN learning and optimal design procedures.

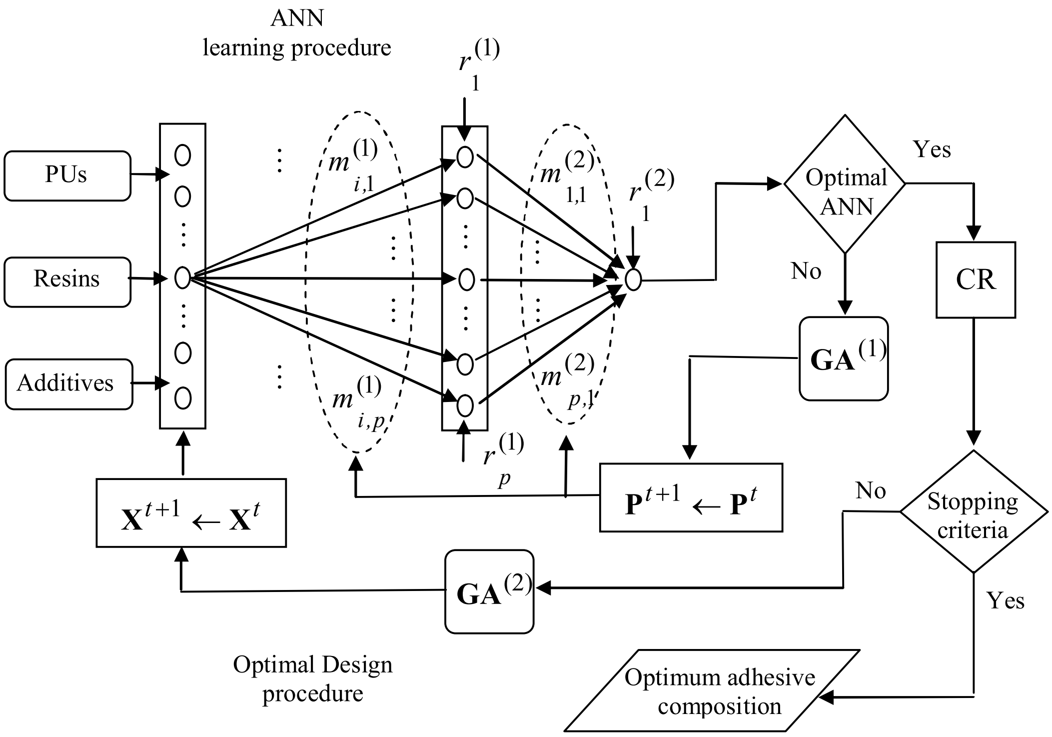

Figure 3. Integrated ANN learning and optimal design procedures.

4.3 First stage: ANN approximation model development

The Artificial Neural Network (ANN) is a nonlinear dynamic system based on a large number of highly interconnected processing units. Its architecture and operating procedures are inspired by our understanding and abstraction on the biological structure of the human brain. This understanding includes attributes such as learning, thinking, memorizing, remembering, rationalizing and problem solving. In the ANN there are processing units or neurons and connections linking these processing units denoted by synapses as in biological sense. A weight value is associated with each connection between processing units that is defined as the connection strength. The weight value acts as a multiplicative filter together with the activation procedure. Learning of ANN occurs while modification of connection weight matrix is undertaken at the learning process. From presented examples or training cases and following an appropriate learning rule the ANN acquires knowledge or relationship embedded in the data. The ANNs are robust models having properties of universal approximation, parallel distributed processing, learning, adaptive behaviour and can be applied to multivariate systems [17, 23].

The proposed ANN is organized into three layers of nodes (neurons): input, hidden and output layers. The linkages between input and hidden nodes and between hidden and output nodes are denoted by synapses. These are weighted connections that establish the relationship between input data and output data. Deviations on neurons belonging to hidden and output layers are also considered in the proposed ANN model. In the developed ANN, the input data vector $\mathbf{D}^{inp}$ is defined by a set of values for design/input variables $\mathbf{x}$, which are the raw materials of the adhesives, such as PU's, resins and additives. In this approach, each set of values for the input variable vector $\mathbf{x}$ is the experimental results as referred in previous sections. The corresponding output data vector $\mathbf{D}^{out}$ contains the creep rate experimental values.

The data used to build the ANN needs to be normalized aiming to avoid numerical error propagation during the learning process. Then the data normalization is done as follows,

$$\underline{D}_k = (D_k - D_{min}) - \frac{D_N^{max} - D_N^{min}}{D_{max} - D_{min}} + D_N^{min} \tag{6}$$

where D_k is the real value of the variable before normalization, D_{min} and D_{max} are the minimum and maximum values of D_k, respectively, in the input/output data set to be normalized. According to Equation (7), the data set is normalized to values $\underline{D}_k$, verifying the conditions

$$D_N^{min} \leq \underline{D}_k \leq D_N^{max} \tag{7}$$

Depending on the input or output data, different maximum and minimum normalized values can be used in Equation (7). The sum of the modified signals (total activation) is performed through the Activation Function. A sigmoid function is applied on each node on hidden layer while a linear function is considered for output layer.

The activation of the *k-th* node of the hidden layer (p=1) or output layer (p=2)and is obtained through sigmoid functions as follows:

$$A_k^{(1)} = \frac{1}{1+e^{-\eta\, C_k^{(1)}}} \tag{8}$$

$$A_k^{(2)} = C_k^{(2)} \tag{9}$$

where $A_k^{(1)}$ and $A_k^{(2)}$ represent the activation functions of the signal of the nodes or neurons of the hidden and output layers, respectively. The signal in each node is $C_k^{(p)}$ defined as the components of the vector $\mathbf{C}^{(p)}$ given by

$$\mathbf{C}^{(p)} = \mathbf{M}^{(p)}\,\mathbf{D}^{(p)} + \mathbf{r}^{(p)} \tag{10}$$

where $\mathbf{M}^{(p)}$ is the matrix of the weights of synapses associated with the connections between input and hidden layer (*p*=1) or between hidden and output layer (*p*=2), $\mathbf{r}^{(p)}$ is the biases vector considered for the nodes of the hidden (*p*=1) or output (*p*=2) layers, $\mathbf{D}^{(p)}$ is the input data vector for the hidden (*p*=1) or output (*p*=2) layer.

The scaling parameters η influence the sensitivity of the sigmoid activation function and must be controlled. The weights of the synapses, $m_{ij}^{(p)}$, and biases in the nodes or neurons at the hidden and output layers, $r_k^{(p)}$, are controlled during the learning process as shown in Figure 3.

The ANN supervised learning is an optimization process based on the minimization of the error between predefined (or experimental) output data and ANN simulated results. In this optimization process the weights of synapses and the biases in neurons are used as design variables. For each set of input data and any configuration of the weight matrix $\mathbf{M}^{(p)}$ and biases $\mathbf{r}^{(p)}$, a set of output results is obtained. These simulated output results are compared with the predefined output values obtained for the same input data to evaluate the difference (or error), which must be minimized during the learning procedure aiming to obtain the optimal ANN configuration.

In the proposed ANN approach several measures of the error are considered with the objective to accelerate and stabilize the learning process. The first measure is the root-mean-squared error defined as

$$RMSE = \frac{1}{N_{exp}} \sqrt{\sum_{i=1}^{N_{exp}} \left(CR_i^{sim} - CR_i^{exp} \right)^2} \tag{11}$$

where N_{exp} is the number of experiments considered in the set of design points of Taguchi and the superscripts *sim* and *exp* denote the simulated and experimental data of creep rate, *CR*. To reinforce the error minimization a second measure is introduced based on the following relative error component:

$$RE = \frac{1}{N_{exp}} \sqrt{\sum_{i=1}^{N_{exp}} \left(\frac{CR_i^{sim} - CR_i^{exp}}{CR_i^{exp}} \right)^2} \tag{12}$$

The influence of the biases of the neurons of the hidden and output layers is also included to stabilize the learning process:

$$\mathbf{\Gamma} = \frac{1}{N_{exp}} \sum_{i=1}^{N_{exp}} \left[\frac{1}{N_{hid}} \sum_{k=1}^{N_{hid}} \left(r_k^{(1)} \right)^2 \right] + \frac{\left(r_1^{(2)} \right)^2}{N_{exp}} \tag{13}$$

The error measures presented from Equations (11) and (12) and biases component in Equation (13) are aggregated using the following formula:

$$F_1\left(\mathbf{M}^{(1)}, \mathbf{r}^{(1)}, \mathbf{M}^{(2)}, \mathbf{r}^{(2)}\right) = c_1\, RMSE + c_2\, RE + c_3\, \mathbf{\Gamma} \tag{14}$$

being the constants c_k used to regularize the numerical differences of the three error terms stabilizing the numerical procedure.

This means that the weights of the synapses and biases can be modified until the value of F_1 fall within a prescribed value. Therefore, the weight of the synapses in matrix $\mathbf{M}^{(p)}$ (p=1,2), and biases of the neurons of the hidden and output layers in vector $\mathbf{r}^{(p)}$ (p=1,2), are modified to reduce the differences (supervised learning) throughout the learning process.

The minimization problem associate to search of the ANN optimal configuration suffers of the same problem of any optimization problem: it can be reach a local minimum. The evolutionary algorithms such as the Genetic Algorithms are more appropriated to search the global optima. Thus, the adopted supervised learning process of the ANN is based on a Genetic Algorithm denoted by $\mathbf{GA}^{(1)}$ [24-26] using the weights of synapses $\mathbf{M}^{(p)}$, and biases of neural nodes at the hidden and output layers $\mathbf{r}^{(p)}$, as design variables as shown in Figure 3. At this stage a population of solutions for ANN configuration denoted by $\mathbf{P}^{(t)}$ is considered at each *t*-generation.

A binary code format is used for these variables. The number of digits of each variable can be different depending on the connection between the input-hidden layers or hidden-output layers. The bounds of the domain of the learning variables and scaling parameter η, is a control parameter. The optimization problem formulation associated with the ANN learning process is based on the minimization of the function defined in Equation (14) without constraints, as follows

$$\text{Maximize } FIT^{(1)} = K^{(1)} - F_1\left(\mathbf{M}^{(1)}, \mathbf{r}^{(1)}, \mathbf{M}^{(2)}, \mathbf{r}^{(2)}\right) \qquad (15)$$

where $FIT^{(1)}$ is the fitness function in GA search to obtain the optimal ANN configuration denoted by $\mathbf{P}_{\text{ANN}}{}^{\text{opt}}$. The constant $K^{(1)}$ must be large enough to obtain always positive fitness values.

4.4 Second stage: optimal design procedure

The optimal design procedure is based on a population of solutions $\mathbf{X}^{(t)}$ updated during the evolutionary search driven by the genetic algorithm, $\mathbf{GA}^{(2)}$. Each solution in $\mathbf{X}^{(t)}$ is ranked according its fitness value, which is related with the objective function and the constraints of the problem defined from equation (1) to equation (5). The fitness value of each solution results from the aggregation of objective value and a graded penalization of constraint violation [24-25]. So, the original optimization problem from equation (1) to equation (5) is transformed as follows:

$$Maximize \quad FIT^{(2)} = K^{(2)} - \alpha_1 \, log\left[CR(\mathbf{x})\right] - \alpha_2 \sum_{i=1}^{N_g} \mathbf{\Phi}_i(\mathbf{x}) \tag{16}$$

with $$\mathbf{\Phi}_i(\mathbf{x}) = \begin{cases} 0 & , \quad \text{if } \varphi_i(\mathbf{x}) \leq 0 \\ R_i \left| \varphi_i(\mathbf{x}) \right|^{q_i} & , \quad \text{if } \varphi_i(\mathbf{x}) > 0 \end{cases} \tag{17}$$

where $\varphi_i(\mathbf{x})$ are the constraints defined from Equation (2) to Equation (4) after normalization. Here, $\varphi_i(\mathbf{x}) \leq 0$ are associated to the feasibility of the constraint $\varphi_i(\mathbf{x})$. The N_g constraints defined from Equation (2) to Equation (4) must be normalized relatively to their bound limits aiming to avoid scaling effects. From equation (16) and (17) it can be established that designs with good fitness and satisfying the constraints have priority in the rank process. Solutions of the problem that violate the constraints are penalized at a graded degree of severity according to the difference between the actual and the allowable values. The constants q_i and R_i are evaluated considering two constraint violation degrees, i.e., strong penalization for large violation value and fair penalization for negligible violation of the constraints [24-26]. The constants α_i are introduced for numerical regularization and $K^{(2)}$ must be large enough to obtain always positive fitness values. The size constraints in Equation (5) are not included in above procedure of penalization. They are imposed directly to the design space at the binary code format transformation used on evolutionary search.

The evolutionary search aiming to solve the minimization problem formulated in equations (16) and (17) is based on the genetic algorithm $\mathbf{GA}^{(2)}$ using appropriate genetic parameters. However, in this case the fitness function of the constrained problem is $FIT^{(2)}$ that depends on design variables vector **x** associated with the raw material constituents used in the composition of the adhesive joint. Since creep rate assumes very small values a logarithmic term of *CR* is considered in the definition of fitness function $FIT^{(2)}$.

4.5 Genetic Algorithm description

The genetic algorithms denoted by $\mathbf{GA}^{(1)}$ and $\mathbf{GA}^{(2)}$ used in both stages of the proposed approach have the same structure but are applied with different genetic parameters selected in independent way.

Genetic algorithms are evolutionary search techniques based on the survival of the fittest and natural selection theory proposed by Charles Darwin. Both proposed $\mathbf{GA}^{(1)}$ and $\mathbf{GA}^{(2)}$ basically performs on three parts: (1) coding and decoding design variables into strings; (2) evaluating the fitness of each solution string; and (3) applying genetic operators to generate the next generation of solution strings in a new population. Four basic genetic operators, namely Selection, Crossover, and Elimination/Replacement from control similarity and Mutation are used in this paper. An elitist strategy based on conservation of the best-fit group transfers the best-fitted solution into a new population for the next generation.

The operators are applied in the following sequence:

- Step1: Initialization. The initial population is randomly generated using a uniform probability distribution function (PDF).

- Step 2: Selection. The population is ranked according to individual fitness. The elite group is determined including highly-fitted individuals. The selection of the couple of parents p_1 and p_2, is fitness-based: one from the best-fitted group (elite) and another from the least fitted one. The current population S^k is transferred to an intermediate stage where they will join the offspring group **B** obtained by the Crossover operator.
- Step 3: Crossover. The crossover operator transforms the couple of chromosomes parents into a new chromosome (offspring) having genes from both progenitors. The offspring genetic material is obtained using the multi-point combination technique known as *parameterized uniform crossover* [25-26]. This is applied to both binary string of the couple selected chromosomes p_1 and p_2. This Crossover is applied with a predefined probability to select the offspring genetic material from the highest fitted chromosome. The offspring group **B** created by the Crossover operator will be joined to the original population S^k generating the enlarged population $S^k \cup \mathbf{B}$.
- Step 4: Elimination/Replacement by similarity control. The enlarged population of solutions $S^k \cup \mathbf{B}$ is ranked according to their fitness. Then, the similarity control is performed gene by gene following an updating scheme during the evolutionary process. The objective is to avoid the presence of very similar individuals into the population reducing the endogamy properties of Crossover operator. This is followed by Elimination of solutions with similar genetic properties and subsequent replacement by new randomly generated individuals. The new enlarged population $S^k \cup \mathbf{B}$ is ranked and the individuals with low fitness are excluded. Now, the dimension of the current population is less than the original one. The original size population will be recovered after including a group of new solutions obtained from the Mutation operator.
- Step 5: Mutation. In the presented approach the Mutation genetic operator is used to overcome the problem induced by Selection and Crossover operators where some generated solutions have a large percentage of equal genetic material. This is associated with a lack of

population diversity inducing premature convergence of the evolutionary process by anchorage at local minima. So, aiming to improve the diversity level a chromosome set group which genes are generated in a random way is introduced into the population. This operation is called *Implicit Mutation* [26] and is quite different from classic techniques where a reduced number of genes are changed. Indeed, this group of chromosomes will be recombined with the remaining individuals into the population during next generations. After mutation, the new population S^{k+1} is obtained and the evolutionary process will continue until the stopping criteria are reached.

- Step 6: Stopping criterion. The stopping criterion used in the convergence analysis is based on the relative variation of the mean fitness of a reference group during a fixed number of generations and the feasibility of the corresponding solutions. This reference group usually is the elite group. The search is stopped if the mean fitness of the reference group does not evolve after a finite number of generations. Otherwise, the population evolves to the next generation returning to Step 2.

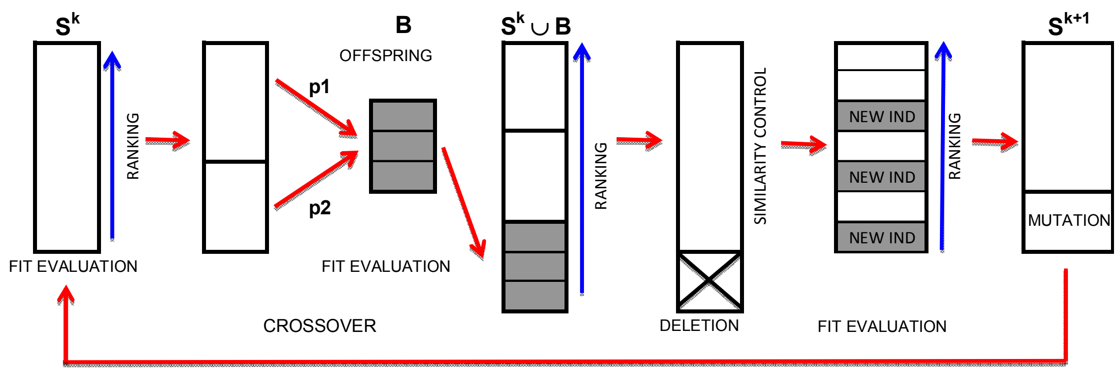

Figure 4. Steps of $GA^{(1)}$ and $GA^{(2)}$ at each *k-th* generation.

Figure 4 shows the flow diagram of the implemented genetic algorithms $GA^{(1)}$ and $GA^{(2)}$. Further details on creating and using a GA for ANN learning can be found in references [24-26].

5. IMPORTANCE ANALYSIS OF DESIGN VARIABLES

The study of the influence of the design variables such as raw material compositions on the structural response of adhesive joint is an important issue. In this approach the importance analysis of design variables is performed based on the Global Sensitivity Analysis (GSA) and supported by variance-based methods [27-29]. The creep rate *CR*, is considered as the measure of structural response of the adhesive joint. On other words, the objective is to measure and to rank the importance of the variability of design variables on the structural response of adhesive joint.

Assuming that the variables are independent, the variance of the conditional expectation $var(E\langle CR|x_i\rangle)$ is used as an indicator of the importance of the design variable x_i on the variance of *CR*. This indicator is directly proportional to the importance of x_i. In particular in this work the first-order global sensitivity index of Sobol [27-29] is used as normalized indicator:

$$S_i^{CR} = \frac{var(E\langle CR \mid x_i\rangle)}{var(CR)} \tag{18}$$

The computational costs to obtain the global sensitivity indices are very important. To overcome this feature the Monte Carlo simulations method is used together Artificial Neural Network (ANN) aiming to estimate the Sobol indices. In this work the GSA is implemented using the optimal network configuration $\mathbf{P}_{\mathrm{ANN}}{}^{\mathrm{opt}}$ obtained at first stage of the proposed optimization strategy. Thus, is possible to avoid the exhaustive and costly experimental tests to obtain the variability of the input variables structural on response.

The methodology to obtain the conditional variances and the system variance is based on the algorithm proposed by António and Hofbauer [19, 29] as follows:

- 1st Step: Lets consider the non-correlated design variables vector **x** following a uniform probability distribution function $Unif(0, 1)$.
- 2nd Step: Considers a set of random numbers $\boldsymbol{\lambda}_{fix}$ following a uniform probability distribution function $Unif(0, 1)$. These N_f random numbers are used to generate the fixed values for the design variable x_i.
- 3rd Step: For each design variable x_i (not for itself) a sample matrix $\mathbf{J}_{\alpha}$ is generated by independently collecting samples of (*p*-1) random numbers following a uniform distribution $Unif(0, 1)$, where the size of the sample is N_r.
- 4th Step: For each design variable x_i a combination of values of $\boldsymbol{\lambda}_{fix}$ and $\mathbf{J}_{\alpha}$ is defined. The structural response of *CR* is evaluated for **x** using the optimal configuration of the artificial network, $\mathbf{P}_{\mathrm{ANN}}{}^{\mathrm{opt}}$. The conditional expectation of structural response is estimated and the mean values of this conditional expectation are calculated. Finally, the variance of the conditional expectation of structural fixing each design variable x_i is estimated. The procedure is repeated for all design variables.
- 5th Step: The variance of structural response $var(CR)$, is estimated considering the previous simulations.
- 6th Step: Calculation of the global Sobol sensitivity index using Equation (18) for all design variables.

6. RESULTS AND ANALYSIS

6.1 Experimental results

To test the proposed approach to adhesive compositions, a several compositions are considered, as shown in Table 2. The Taguchi design points used to plan the experiments are considered as input values in the ANN learning procedure. A number of 27 training data sets are selected inside the interval domain of each design (random) variable and levels defined in Table 2.

Table 2. Materials used in adhesive joint and Taguchi levels definition.

Raw Materials		Real value levels
Polyurethanes (PU's):		
1.	**Caprolactone with extremely high crystallization**	2.5/5/10
2.	**Polyester with extremely high crystallization**	2.5/5/10
3.	**Polyester with very high crystallization**	2.5/5/10
Resins:		
4.	**Colophony WW**	0/0.2/0.5
5.	**Hydrocarbon (C9)**	0/0.2/0.5
6.	**Alkyl phenolic**	0/0.2/0.5
7.	**Terpene phenolic**	0/0.2/0.5
8.	**Coumarone-Indene**	0/0.2/0.5
9.	**Vinyl Chloride / Acetate Vinyl**	0/0.2/0.5
Additives:		
10.	**Fumaric Acid**	0/0.3/0.6
11.	**Hydrophobic silica**	0/1/2
12.	**Nitrocellulose**	0/1/2
13.	**Chlorinated rubber**	0/1.5/3
Constraints:		**% weight on formula**
Total % PU		10-20
Total % Resins		0-1
Total % Additives		0-7

The Taguchi values are selected according to the approach proposed by Taguchi and Konishi [22]. By the selected Taguchi table L27(3^{13}) the actual composition for each Taguchi design point is obtained, as shown in Table 3. The values presented in Table 3 and Table 4 are used as input/output patterns for learning procedure of ANN.

On an initial analysis, when confronted Tables 3 and 4, we can see that maximizing the amount of colophony and hydrocarbon resin on the adhesive composition, we obtain a very high creep rate. We can see that the amount of chlorinated rubber decrease the creep rate. And, if the anterior conditions were respected, if we add phenolic resins to the formulation we can minimize the creep rate. These features show the needs to implement an optimization procedure.

Table 3. Taguchi design points: % weight on formulation (design variables values).

Design point	Material number												
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**
1	2.5	2.5	2.5	0	0	0	0	0	0	0	0	0	0
2	2.5	2.5	2.5	0	0.2	0.2	0.2	0.2	0.2	0.3	1	1	1.5
3	2.5	2.5	2.5	0	0.5	0.5	0.5	0.5	0.5	0.6	2	2	3
4	2.5	5	5	0.2	0	0	0	0.2	0.2	0.3	2	2	3
5	2.5	5	5	0.2	0.2	0.2	0.2	0.5	0.5	0.6	0	0	0
6	2.5	5	5	0.2	0.5	0.5	0.5	0	0	0	1	1	1.5
7	2.5	10	10	0.5	0	0	0	0.5	0.5	0.6	1	1	1.5
8	2.5	10	10	0.5	0.2	0.2	0.2	0	0	0	2	2	3
9	2.5	10	10	0.5	0.5	0.5	0.5	0.2	0.2	0.3	0	0	0
10	5	2.5	5	0.5	0	0.2	0.5	0	0.2	0.6	0	1	3
11	5	2.5	5	0.5	0.2	0.5	0	0.2	0.5	0	1	2	0
12	5	2.5	5	0.5	0.5	0	0.2	0.5	0	0.3	2	0	1.5
13	5	5	10	0	0	0.2	0.5	0.2	0.5	0	2	0	1.5
14	5	5	10	0	0.2	0.5	0	0.5	0	0.3	0	1	3
15	5	5	10	0	0.5	0	0.2	0	0.2	0.6	1	2	0
16	5	10	2.5	0.2	0	0.2	0.5	0.5	0	0.3	1	2	0
17	5	10	2.5	0.2	0.2	0.5	0	0	0.2	0.6	2	0	1.5
18	5	10	2.5	0.2	0.5	0	0.2	0.2	0.5	0	0	1	3
19	10	2.5	10	0.2	0	0.5	0.2	0	0.5	0.3	0	2	1.5
20	10	2.5	10	0.2	0.2	0	0.5	0.2	0	0.6	1	0	3
21	10	2.5	10	0.2	0.5	0.2	0	0.5	0.2	0	2	1	0
22	10	5	2.5	0.5	0	0.5	0.2	0.2	0	0.6	2	1	0
23	10	5	2.5	0.5	0.2	0	0.5	0.5	0.2	0	0	2	1.5
24	10	5	2.5	0.5	0.5	0.2	0	0	0.5	0.3	1	0	3
25	10	10	5	0	0	0.5	0.2	0.5	0.2	0	1	0	3
26	10	10	5	0	0.2	0	0.5	0	0.5	0.3	2	1	0
27	10	10	5	0	0.5	0.2	0	0.2	0	0.6	1	2	1.5

Table 4. Creep rate [mm/min] for Taguchi design points obtained by experiments.

Design point	Creep rate	Design point	Creep rate	Design point	Creep rate
1	0.0842	**10**	0.1588	**19**	0.0204
2	0.1545	**11**	0.0778	**20**	0.0290
3	0.7000	**12**	0.3344	**21**	0.0291
4	0.1341	**13**	0.0570	**22**	0.0950
5	0.1551	**14**	0.1442	**23**	0.1061
6	0.0966	**15**	0.0569	**24**	0.0579
7	0.6333	**16**	0.0349	**25**	0.0213
8	0.0433	**17**	0.0254	**26**	0.0305
9	0.0840	**18**	0.0178	**27**	0.1195

6.2 First stage: results and analysis of ANN learning procedure

According Table 2 a number of 13 raw materials are considered as input parameters against 1 output parameter, the creep rate *CR*. A number of 8 neurons are considered for the hidden layer of the ANN topology described in section 4.2 and section 4.3. The ANN learning process is formulated as an optimization problem based on maximization of fitness $FIT^{(1)}$ defined in Equation (15). The ANN learning process is performed by $\mathbf{GA}^{(1)}$ using a population $\mathbf{P}^{(t)}$ with 30 individuals in evolutionary search. The elite and mutation groups of $\mathbf{GA}^{(1)}$ have 9 and 3 individuals/solutions, respectively [24-26]. The binary code format with five digits is adopted for weights of synapses and biases of neural nodes at both input-hidden and hidden-output linkages. The ANN learning process is concluded after 30.000 generations. The constants in Equation (14) are $c_1 = 5000$, $c_2 = 1000$ and $c_3 = 1$. The constant $K^{(1)} = 5.\times 10^5$ is select for fitness function $FIT^{(1)}$ in Equation (15).

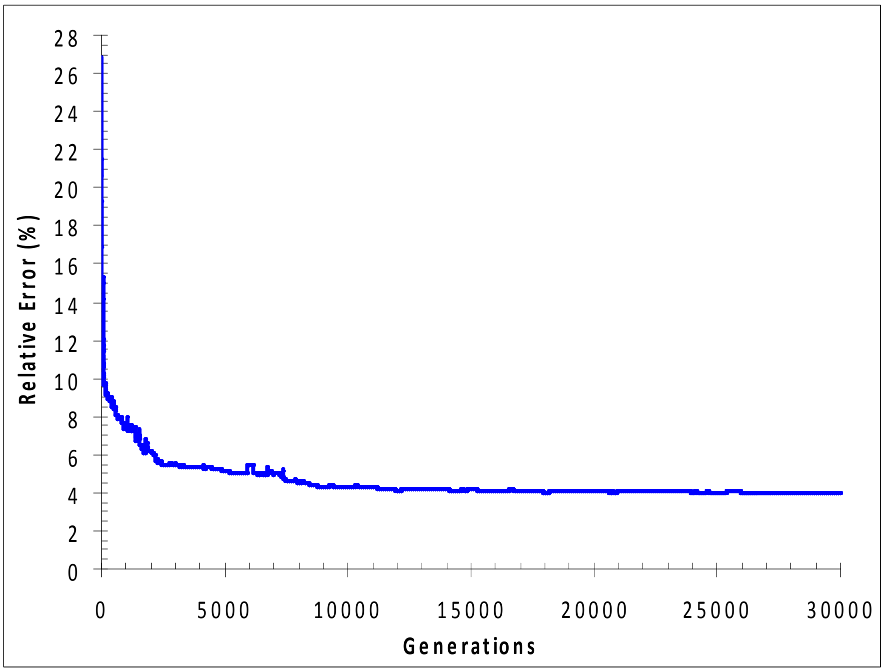

Figure 5. Evolution of mean relative error at ANN learning process based on GA (1) .

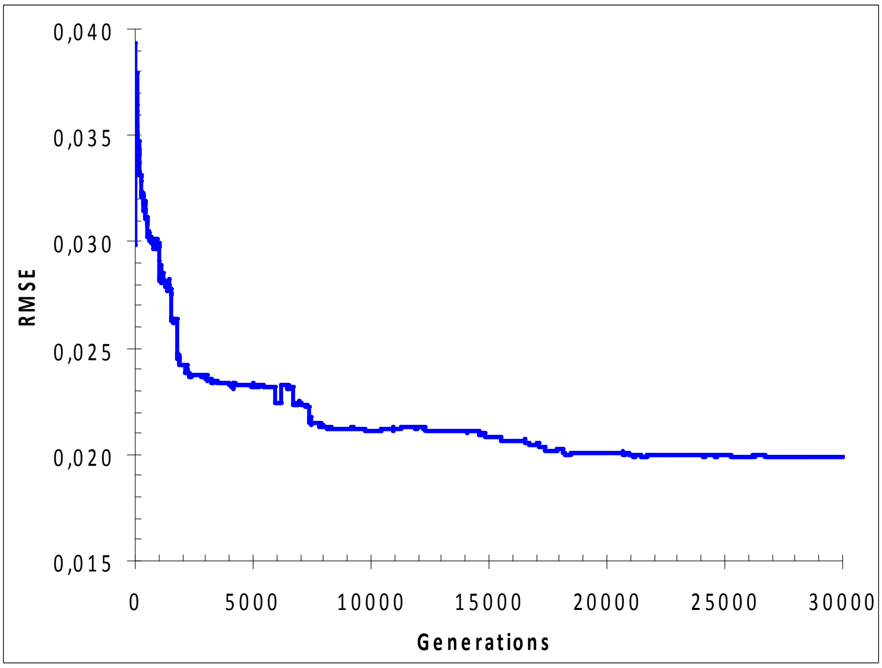

Figure 6. Evolution of root-mean squared error at ANN learning process based on GA (1) .

Figures 5 and 6 show the evolution of the error parcels at ANN learning process based on $\mathbf{GA}^{(1)}$ along first stage of the proposed optimization strategy. Those error components were defined in Equation (11) and Equation (12). The relative error of 4.00% is reached for optimal configuration $\mathbf{P}_{\mathrm{ANN}}{}^{\mathrm{opt}}$ of the developed ANN.

6.3 Second stage: results and analysis of the optimal design procedure

The optimization procedure during the second stage corresponds to constrained minimization of creep rate, C*R* as defined from Equation (1) to Equation (5). That original optimization problem is transformed for evolutionary search format in Equation (15) and Equation (16). The fitness function $FIT^{(2)}$, depends on design variable vector **x** associated with the raw material constituents used in the adhesive formulation. The fitness evaluation is based on optimal configuration $\mathbf{P}_{\mathrm{ANN}}{}^{\mathrm{opt}}$ of the ANN obtained at the first stage of the proposed optimization strategy approach as shown in Figure 3.

The optimization problem of creep rate minimization is solved with imposition of technological constraints defined from Equation (2) to Equation (4). The constraints in those equations are normalized as previously referred in Section 4.4. The constants q_i and R_i in constraint terms on Equation (16) and Equation (17) are calculated considering two constraint violation degrees, as follows:

- a penalization equal to 100 for strong violation value equal to 0.1;
- a penalization equal to 1 for fair violation value equal to 0.01 .

The constants $\alpha_1 = 10$, $\alpha_2 = 1.$ and $K^{(2)} = 4.\times 10^4$ are select for fitness function $FIT^{(2)}$ defined in Equation (16).

The constrained evolutionary search based on $\mathbf{GA}^{(2)}$ is performed using a population $\mathbf{X}^{(t)}$ with 21 individuals. The elite and mutation groups of $\mathbf{GA}^{(2)}$ have 7 and 4 solutions, respectively [24-26]. A binary code format with 4 digits is adopted. A number of 5000 generations was considered in evolutionary search performed by $\mathbf{GA}^{(2)}$ on to this second stage of the proposed optimization strategy approach. Figure 7 shows the behaviour of creep rate *CR*, during the second stage. An improvement of 99.3% relatively to the best initial value was reached and the corresponding optimal solution is shown in Figure 8.

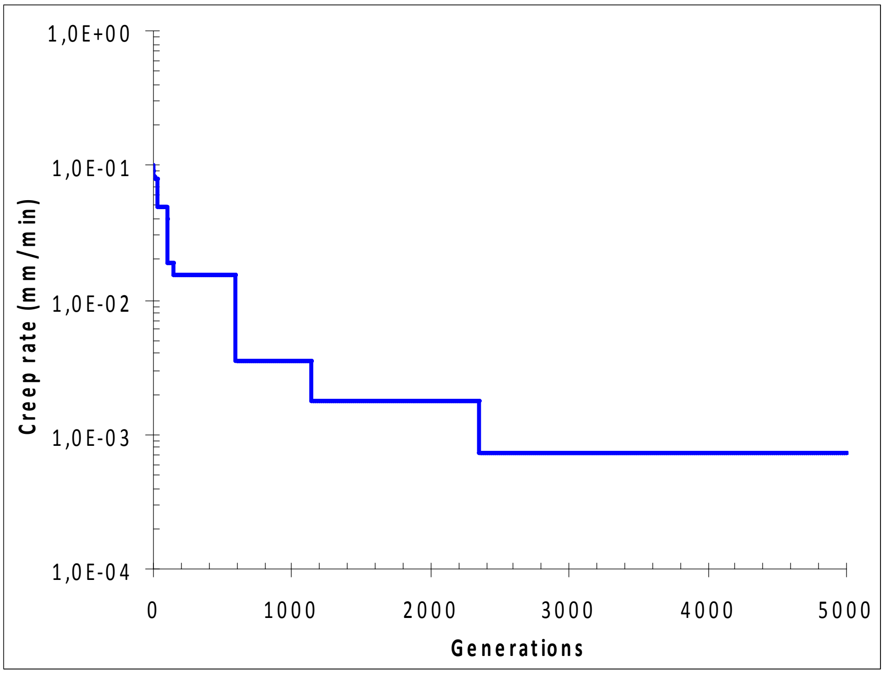

Figure 7. Evolution of creep rate constrained minimization during $\mathbf{GA}^{(2)}$ search.

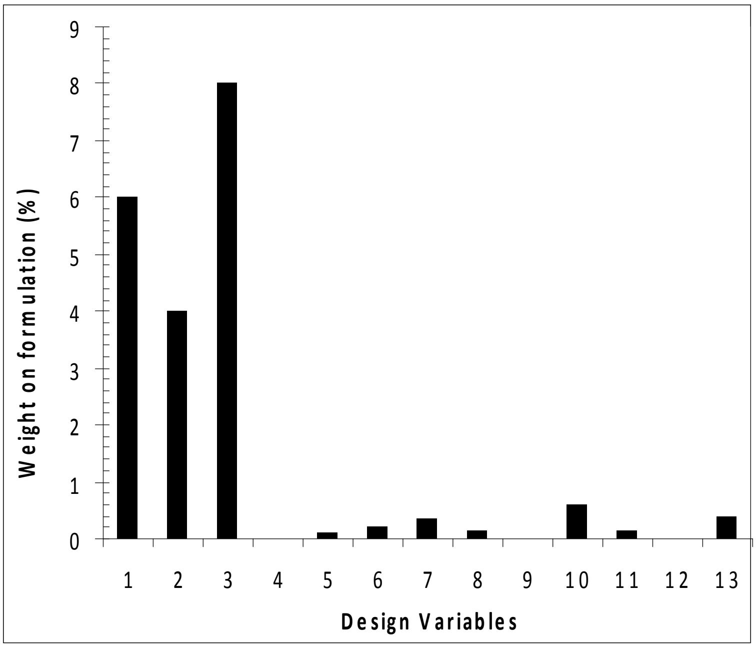

Figure 8. Optimal solution values for composition of the adhesive joint.

Figure 8 shows the optimal values of raw material constituents of adhesive joint obtained after the second stage of the proposed optimization strategy approach.

The calculation for the solution gives the following sum values:

Total % PUs=18.0 %; total % Resins=0.80%; total % Additives=1.13%.

Those are fallen inside the constraint intervals presented in Table 2.

The optimal result obtained for creep rate minimization based on proposed approach is consistent with the experimental testing data used to implement the model. Indeed, the creep rate is minimized when large quantities for PUs and for some additives are considered, and when colophony and vinyl resin aren't considered on the formulation, as shown in Table 3 and Table 4 for definition of Taguchi design points.

The use of the $\mathbf{P}_{\mathrm{ANN}}{}^{\mathrm{opt}}$ obtained at the end of first stage of the proposed approach enables to search all promising regions of the design space at the second stage of the procedure. On contrary, by the planning of experiments based on Taguchi technique, only discrete points can be considered. So, comparing the results of Figure 8 (optimization) with the ones in Table 4 (experimental), it is possible to conclude that the creep rate values from optimization process (7.39×10^{-4}) are less than the minimum obtained from experimental tests (1.78×10^{-2}) and presented on Table 4.

6.4 Experimental validation of results

Experimental tests are implemented using the optimal design values presented in previous section. The weight formulations (%) of raw materials corresponding to the optimal solution as shown in Figure 8 are considered to build the test pieces for the experimental validation. The complete creep rate experimental test curve is shown in Figure 9. The observed failure happens in the tertiary phase and was cohesive.

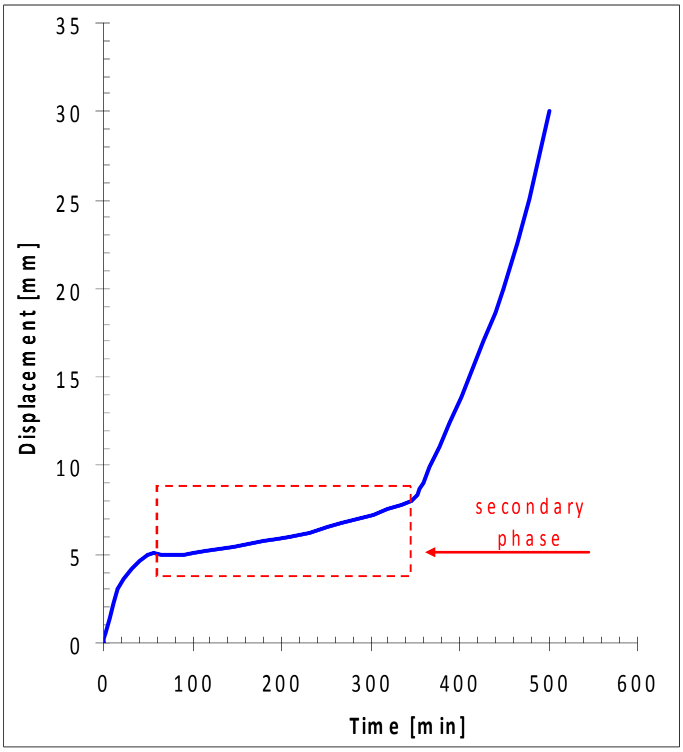

Figure 9. Creep rate experimental test curve (complete) obtained for the optimal solution with composition presented in Figure 8.

Since the primary and the tertiary phase are ignored on the calculation of the mean of the separation lengths of the bond only the secondary phase in curve plotted in Figure 9 is considered to evaluate the creep rate as referred in Section 3.2. The detailed part of the creep rate experimental test curve for the second phase is shown in Figure 10. The slope of the line obtained by linear regression of the experimental results corresponds to the creep rate [21]. This experimental value is equal to 0.0137 mm/min, which is greater than the numerical one, CR=0.000739 mm/min obtained after the optimization process plotted in Figure 7.

From the analysis of both results it can be concluded on the uncertainty of the experimental assessment of CR. These uncertainties are extensive to the experimental results on Table 4 for Taguchi design points. Since the learning procedure of the ANN used in optimization procedure depends on the experimental results considered for Taguchi design points the differences of CR values after validation are explained.

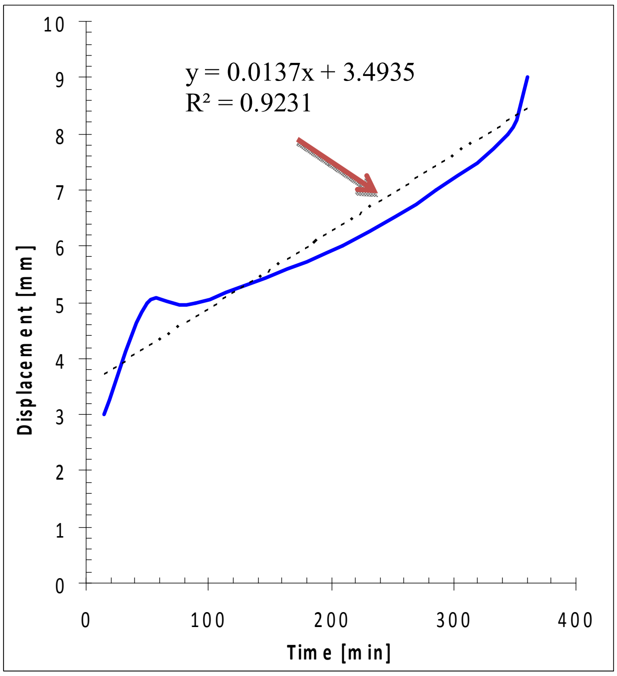

Figure 10. Creep rate experimental test curve - secondary phase, obtained for the optimal solution with composition presented in Figure 10. Linear regression of experimental values is plotted.

Since the uncertainty in creep rate experimental assessment is taken into account these validation results for creep rate of adhesive joints are quite similar to the ones obtained using the proposed two-stage ANN-GA optimization approach showing the capabilities of this numerical model.

6.5 Results of importance analysis of design variables

According the flow diagram of the proposed approach presented in Figure 1 a ANN-based Monte Carlo simulation procedure is implemented aiming to study the variability of the structural response of the adhesive joint. In particular the Sobol indices based on GSA are used to establish the relative importance of the design variables [8], [17-19]. The GSA indices are obtained through ANN-Monte Carlo approach based on the algorithm described in Section 5. In this algorithm the values $N_f = 50$ and $N_r = 100$ are used to obtain the conditional probability for Sobol index. Two sampling procedures are simulated using the optimal $\mathbf{P}_{\mathrm{ANN}}{}^{\mathrm{opt}}$. The contribution of the variance of the conditional expectation, $var(E\langle CR|x_i\rangle)$, for the total variance of creep rate, *var*(C*R*) is calculated based on those sampling procedures. After, one first-order Sobol index per design variable x_i is obtained using the equation (18).

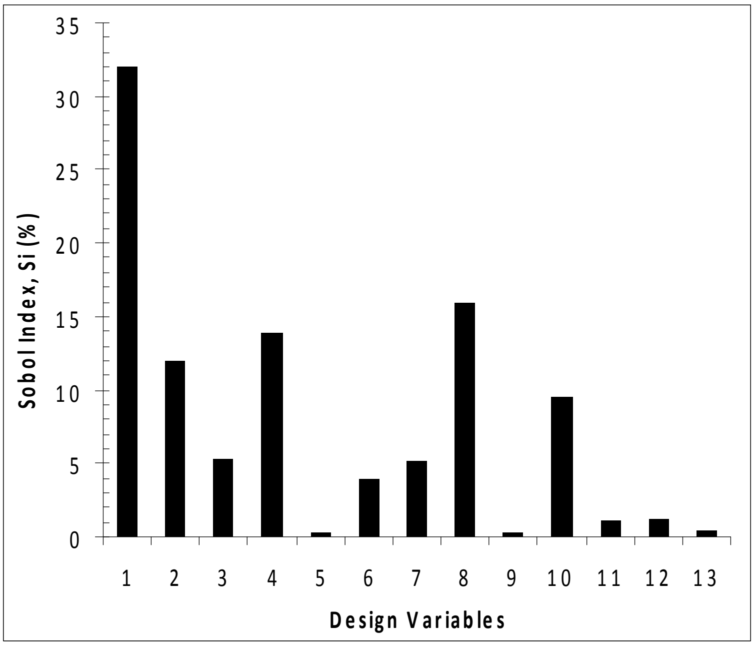

Figure 9. Importance of the design variables measured by first-order Sobol index S_i^{CR}.

The histograms in Figure 9 show the importance of the design variables measured by first-order Sobol index S_i^{CR}. They represent the contribution (%) of the variance of the conditional expectation, $var(E\langle CR|x_i\rangle)$, for the total variance of creep rate, *var*(C*R*). The design variables are the solid raw material constituents such as PUs, resins and additives, such as are identified in Table 2.

The performance measured by creep rate of the adhesive joint is very sensitive to the influence of some polyurethanes (materials 1 and 2), and a particular sensitivity to caprolactone type with extremely high crystallization is observed. The sensitivities of the creep rate to the resins Colophony (material 4) and Coumarone-Indene (material 8) are also important. However, in relation to the colophony, the sensitivity is in the negative direction, which means that it is a resin that affects negatively the creep rate of the adhesive composition of the adhesive joint. This is the reason why the results obtained in second stage of the optimization strategy did not consider the colophony in the optimal solution as shown in Figure 8.

Although the contribution of the additives is related with the improvement of mechanical behavior of PUs and resins, their influence on creep rate is shown through the sensitivity of Fumaric Acid (material 10). On contrary, the influence of Chlorinated rubber (material 13) is not explained directly attempting to low creep rate sensitivity relatively to this material.

The GSA results in Figure 9 can help the designer to decide on the most important design variables to be considered for the optimization in second stage of the procedure. Furthermore, the GSA at the first stage when combined with the ANN-GA optimization process at second stage, can be a powerfully tool to take decisions on the optimal solutions applied to the composition of adhesive joints.

7. CONCLUSIONS

An approach capable to predict and optimize the creep rate of the footwear adhesive joint, based on the composition of adhesive joints was presented. The proposed approach is based on two stages: (i) definition of the physical model based on planned experimental measurements and development of the ANN approximation model; (ii) the optimization algorithm that is the engine search of the optimal design the composition of adhesive joints.

First of all, the set of experiments are planned using the Taguchi method aiming to obtain a good representation of the physical phenomenon. Secondly, considering the experimental results obtained for Taguchi design points as input/output patterns, an Artificial Neural Network (ANN) is developed based on supervised evolutionary learning using a GA. Secondly; the optimal design of adhesive composition to achieve the target of minimum creep rate under manufacturing constraints is proposed. During this last optimization process the solutions are evaluated using the optimal ANN previously obtained.

Finally, inside the optimization strategy a ANN-based Monte Carlo simulation procedure is implemented aiming to study the sensitivity of the structural response of adhesive joint relatively to design variables. In particular the Sobol indices for global sensitivity analysis are used to establish the relative importance of the design variables.

The results show the robustness of the proposed approach to predict and optimize the creep rate properties of the footwear adhesive joint using the raw material constituents as design variables. The optimal results for creep rate minimization based on proposed approach are reached when large quantities for PUs and for some additives are considered, and when colophony and vinyl resin aren't considered on the formulation. The performance measured by creep rate of the adhesive joint is very sensitive to the influence of some PUs (materials 1 and 2), and a particular sensitivity to caprolactone type with extremely high crystallization is observed. The sensitivities of the creep rate to the resins Colophony (material 4) and Coumarone-Indene (material 8) are also important

The proposed optimization strategy supported by experimental tests shows improved explorative properties of design space and can be a powerfully tool for the designers of adhesive joints in footwear industry.

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Compliance with Ethical Standards

The authors declare that they have no conflict of interest.

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PAPER 7

MULTI-OBJECTIVE OPTIMIZATION: PEEL STRENGTH AND CREEP RATE

MULTIOBJECTIVE OPTIMIZATION OF MECHANICAL PROPERTIES BASED ON THE COMPOSITION OF ADHESIVES

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ABSTRACT

A mixed numerical-experimental approach capable to predict and optimize the performance of the footwear adhesive joints, based on the weight composition of used raw materials was presented. The approach based on the optimal design of adhesive composition to achieve the targets of minimum creep rate (CR) and maximum peel strength (PS) under manufacturing. Two stages are considered in the proposed approach. In the first stage, an approximation model is built based on planned experimental measurements and artificial neural network (ANN) developments. The ANN learning procedure uses a genetic algorithm. In the second stage an optimal design procedure is developed based on multi-objective design optimization (MDO) concepts. The MDO algorithm based on dominance concepts and evolutionary search is proposed aiming to build the optimal Pareto front. The model uses the optimal ANN to evaluate the fitness functions of the optimization problem. Furthermore, a ANN-based Monte Carlo simulation procedure is implemented and the sensitivity of the creep rate and peel strength relatively to weight compositions of raw materials is determined.

The approach shown robustness to establish the trade-off between minimum creep rate properties and minimum inverse peel strength (maximum peel strength) using the weight composition of used raw materials. The optimal results for both CR and PS based on proposed approach are reached when large quantities for polyurethanes (Pus) and for some additives are considered. The performances of adhesive joints measured by CR and PS are very sensitive to the influence of some PUs and in some way are moderately sensitive to additives. The proposed MDO approach supported by experimental tests shows improved explorative properties of raw materials and can be a powerfully tool for the designers of adhesive joints in footwear industry.

Key-words: Multi-objective optimization, footwear adhesive joints, creep rate, peel strength, ANN, dominance, genetic algorithm.

1. INTRODUCTION

The adhesives are one of the most important bonding methods of assembling shoes components. The application of adhesives to bond materials allows simplify the steps production on footwear when drastically reduced the number of production operations. Since 1970, the polyurethane (PU) adhesives solvent based was introduced to manufacture shoes because of its ability to bond a wide variety of materials [1-4].

Depending on the materials used for the sole and for the upper, various pretreatments could be needed to improve the bond [5-6]. Proper surface treatment is the key to obtaining good adhesive bonds, allowing removing dirt, grease, mod-release agents, processing additives, plasticizers, protective oils and other contaminants that could compromise the bonds [6].

There are available a lot of surface treatments, in this work will be considered the primer, mechanical and chemical treatments [2, 6]. Mechanical and chemical treatments are methods that aim to modification the surface to enhance the adhesive forces for high demands on bonded joints [7-9]. The application of primer are also used in conjunction with a surface treatment either to improve adhesion performance [6, 9]. Primers consist in a solution of polymers in organic solvents that, in their composition, are related to the adhesive [8-13].

PU is largely used for adhesives owing to their outstanding properties [2, 10]. These types of adhesives are characterized because of their excellent adhesion, flexibility, low-temperature performance, high cohesive strength and cure speed [14-16]. The formulation is based on thermoplastic PU resins [16], fillers, resins, solvents and in some cases it is used catalysts as a crosslinking agent [5, 9, 16]. Fillers are used to improve physical properties, like viscosity, temperature resistance, stability, under lower cost. In this work it will be considered the fumaric acid, silica, nitrocellulose and chlorinated rubber [2, 9]. Resins are usually used to increase tack and temperature resistance to the adhesive. In this work will be considered colophony, hydrocarbon, alkyl phenolic, terpene phenolic, cumarone-indene and vinyl chloride/acetate vinyl types of resins [9, 13-16]. Solvents are mainly esters and ketones. The total solvent portion ranges is between 75% and 85% [16].

The PU adhesives available systems are classified as one-component and two-component systems [9, 14-15]. The one-component system consists in an adhesive formulated with several components mixed and stored together [9]. The two-component system consists in an adhesive and a catalyst stored separated, they are mixed just before the application because of their short pot life. In this system the cure develop rapidly between the poliol of the PU resin present on the adhesive and the NCO group of the catalyst (isocyanate type) [9, 14]. The two components systems are used when heat resistance is required [9].

In PU adhesives solvent-based, after the evaporation of the solvent, heat and pressure are applied to melt the polymer and press the parts for adhesion, contributing to the crosslinking [7-9, 16]. So, for bonding the sole, the adhesive film is activated by IR irradiation by 2-6 seconds, at 55-80 ºC. Upon cooling the adhesive recrystallizes to give a strong and flexible bond [7-9].

In the footwear industry, the manufacture of the shoes, for assembling the sole to the upper, follow some steps as show on the Figure 1. Each individual process step is important for the quality of the bonded product [7,8]. Indeed, the selection of the weight composition of raw materials plays an important role aiming to manufacture the best adhesive joint, allowing accomplishing the demands of the customers.

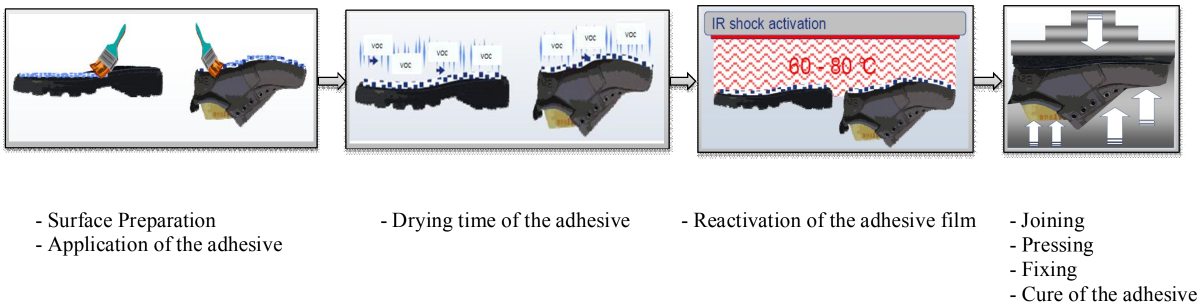


Figure 1. Application of PU adhesive solvent based and the individual steps on the assembling process.

On other hand the creep rate and the peel strength are the most important mechanical properties for quality requirements of the adhesive joints to be considered in the footwear industry [5,9]. So, it is intended to develop a model capable to predict and optimize the creep rate and the peel strength depending on the composition of the raw materials used in the adhesive joint [9].

2. PROBLEM DEFINITION AND DESIGN APPROACH

To manufacture the shoes, in this work it is considered the natural leather as material for the upper and the thermoplastic rubber (TR) as material for the sole. It is necessary to consider surface treatment on the materials to increase the mechanicals properties, so, physical and chemical surface treatments are applied such as mechanical carding and halogenations, respectively [7-9, 11-

12]. The adhesive formulation is composed of a number of substances giving certain mechanical properties to final adhesive depending on the substrates that are part of the adhesive joint [8, 13]. The aim of this work is to develop a model where the design variables are the inputs on the solid raw materials that compose the formulation of the adhesives and the outputs are the mechanical properties of the manufactured adhesive joint. Therefore, it is considered the PU adhesives because their excellent adhesion. So, the design variables are the constituents such as polyurethanes (PUs), resins (REs) and additives (ADs) [8].

The responses of the adhesive joint are measured by their mechanical properties, the creep rate and the peel strength. The peel strength is associated with the strength of bonded product and the creep rate is associated with the performance properties for temperature resistance of adhesives. So, both mechanical properties should be considered as measures of the quality of the adhesive joint in footwear industry.

In general, the peel strength must be maximized and the creep rate must be minimized satisfying the size or technological requirements. So, the optimal design depends on the constrained multi-objective optimization of both mechanical properties of the adhesive joint. Since, both objectives appear contradictory a Pareto front must be built aiming to find the trade-off between solutions minimizing creep rate and maximizing peel strength.

The proposed strategy for the multi-objective design optimization (MDO) of creep rate and peel strength is based on three columns as follows: 1. the construction of physical model representation; 2. the adopted multi-objective optimization algorithm; and 3. the architecture of the optimization model connecting the different modulus.

The first column of the proposed optimization strategy is the definition and construction of the physical model representing the adhesive joint of footwear product and the relationship between the design variables – the weight composition of raw materials, and the inherent structural response measured by creep rate and peel strength. The proposed approach for this first column is based on planned experimental measurements and using these testing results to develop the approximation model. First of all, the set of experiments are planned using the Taguchi method aiming to obtain a good coverage of the design space for the composition of the adhesive joint. Secondly, considering the experimental results obtained for Taguchi design points as input/output patterns, an Artificial Neural Network (ANN) is developed based on supervised evolutionary learning [17-19]. This ANN learning procedure is equivalent to solve an optimization problem where the difference between the experimental results and the ones obtained from the ANN is minimized controlling the ANN parameters.

The second column of the optimization strategy is the multi-objective design optimization (MDO) algorithm used in the constrained optimal design search based on creep rate minimization and peel strength maximization. A Genetic Algorithm based on dominance concepts is adopted supported by short and enlarged populations of solutions.

The third column of the optimization strategy is the architecture of optimization model connecting the different modulus collecting data necessary for multi-objective optimization algorithm which comes from the optimization problem formulation. A multi-objective approach based on the optimal design of adhesive composition to achieve the target of minimum creep rate and maximum peel strength under manufacturing constraints is proposed. During the optimization process the solutions are evaluated using the optimal ANN built in the first column of optimization strategy.

Inside the third column of the optimization strategy at the end of ANN optimal configuration search a ANN-based Monte Carlo simulation procedure is implemented aiming to study the sensitivity of the structural response of adhesive joint relatively to design variables of the MDO process. In particular the Sobol indices for global sensitivity analysis are used to establish the relative importance of the design variables [18, 19]. Figure 2 shows the flow diagram referring the three columns of the proposed MDO approach.

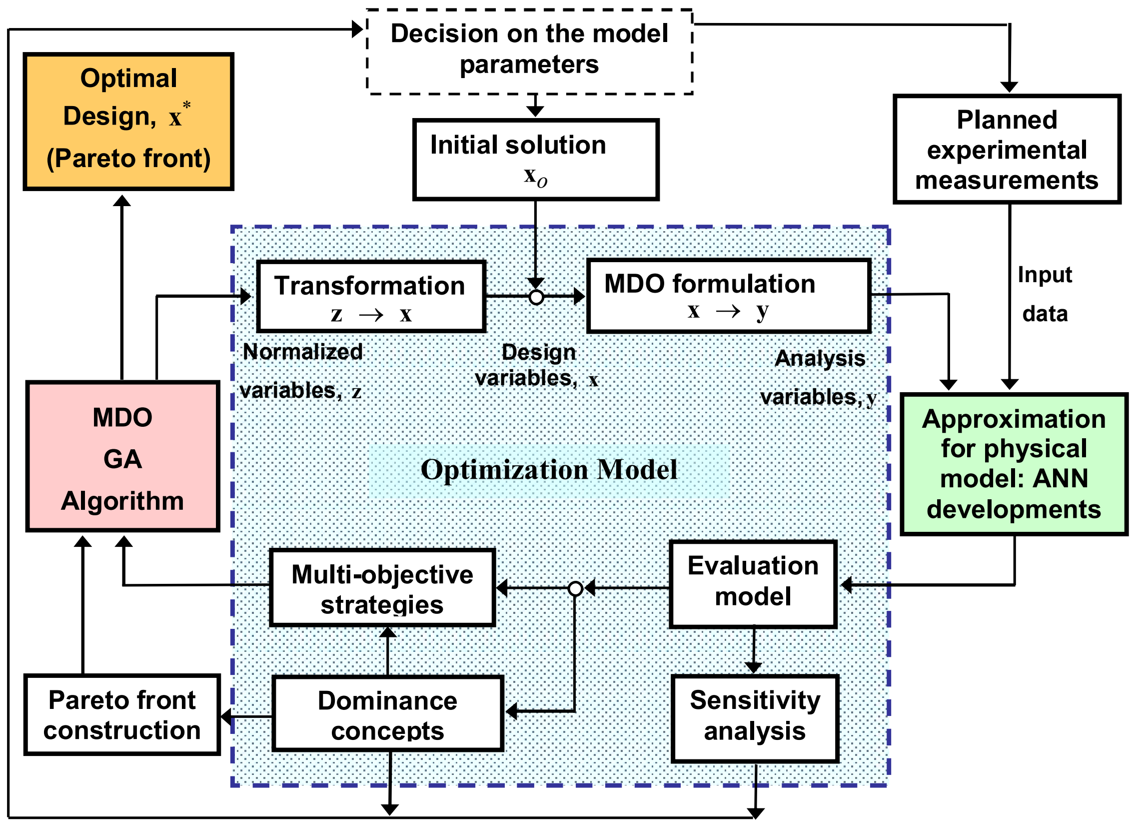


Figure 2. Flow diagram of the proposed MDO approach for footwear adhesive joints.

3. EXPERIMENTAL TESTS

The proposed approach for the first column of the optimization strategy is based on planned experimental measurements necessary for the development of the approximation model. So, a set of experiments are implemented aiming to obtain data used in learning procedure of generation of the approximation model defining the behaviour of adhesive joint.

3.1 Materials

The TR material considered in this work is TTSC TR-2531-80C. The properties of this material were provided by the manufacturer of the sole (technical datasheet of the material) and are presented in Table 1. The Halinov 2190 [20] is used as halogenate for TR. The Plastik 6271 [20] is selected as a primer for the leather, an adhesive primer usually is a diluted solution of an PU adhesive in an organic solvent [8-9] which depends on the nature of the substrate surface [11]. The Cipadur 2230T [20] is applied as crosslinker to increase temperature resistance, in a dosage of 5% of the adhesive trials planned by the Taguchi method.

Table 1. Physical properties of the TTSC TR-2531-80C.

Physical properties	Method	units	Sonaflex TTSC-2531-80C
Density	ASTM D792	g/cm^3	0.92 – 0.98
Hardness	DIN 53505	Shore A	77 – 83
Tensile	DIN 53504	MPa	≥ 4
Elongation at rupture	DIN 53504	%	≥ 300
Abrasion resistance	DIN 53516	mm^3	≤ 250
Flexion resistance	BS 5131:2.1 (150000 cycles)	mm/Kc	< 0.1

The TR material considered in this work is TTSC TR-2531-80C. The properties of this material were provided by the manufacturer of the sole (technical datasheet of the material) and are presented in Table 1.

3.2 Experimental techniques

Taking into account the composition of adhesives this work focuses on creep rate and on peel strength measurements aiming to evaluate the mechanical behaviour of the PU adhesive solvent-based when bonding natural leather uppers to TR soles.

The creep rate (CR) is a property that determines the resistance to peeling by a constant load of the single lap joint stored at an elevated temperature [9, 21]. The principle of the creep test is suspending the test specimen in a heated cabinet with a constant peeling strength applied between the two adherents. After a set time it's measured the bond separation.

Peel strength (PS) is a property which determines the strength required to peel of two materials. This test enables to distinguish if an adhesive is fragile or ductile [7-9, 21]. The principle of the peel test is the peeling of the test specimen using a tensile machine while the force required to separate the two adherents is measured.

Both methods are applicable to joints where at least one of the adherents is flexible. To quantify these properties are tested with a standard test [21]. The standard norm used for footwear industry adhesives is described on the EN 1392:1998 [21]. This standard norm allows obtaining the creep rate in variation of displacement per unit of time. On other hand, the standard norm allows obtaining the peel strength per unit width, which is the average load per unit width, applied at an angle between 90° and 180°, depending on the flexibility of the substrate in relation to the joint needed to lead to failure [21].

3.2.1 Preparation of the single lap joint:

The application of the surface treatment depends on the materials that are intended to be bonded. On the leather is necessary to apply a surface treatment, which is the mechanical treatment, and a primer to improve a surface interaction between adhesive and the adherent [6-9, 11]. A P24 aluminum oxide abrasive cloth is used for the mechanical treatment. The primer is applied and allowed to dry for at least 10 minutes at room temperature [7-9]. It is necessary to consider a chemical treatment as a surface treatment on TR. In this work it is used a halogenated agent and allowed to dry at least 1 hour at room temperature [7-8, 12].

After the surface treatment of the adherents, the adhesives experiments planned by the Taguchi method are applied on both substrates and allowed to dry for 15 minutes at room temperature. To manufacture the single lap joints the adhesive films are activated by Infrared (IR) radiation at temperature of about

70 °C and during 6 seconds. The substrates are bonded in the desired position, as seen in Figure 3, and the adhesive joint is subjected to a pressure of 4 bars during 5 seconds. The adhesive joints, after being pressed, are stored in standard conditions (23 ºC, 50% Hr) during 72h, in order to ensure the complete cure of the adhesive [7-9].

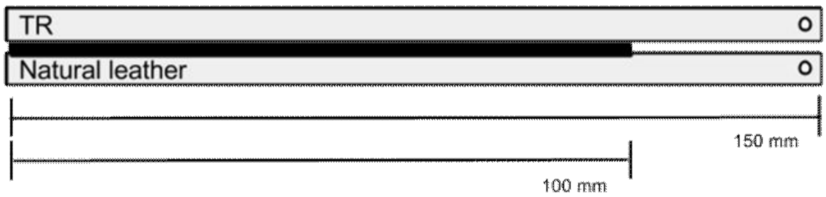
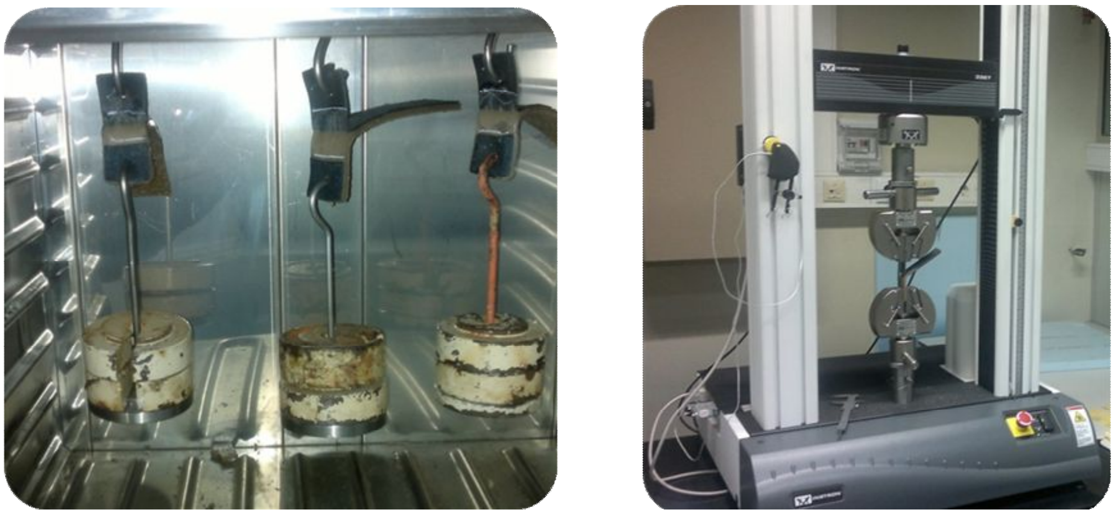


Figure 3: Test piece geometry.



a) **b)**

Figure 4: a) Creep rate test; b) Peel strength test.

The adhesive joint studied is composed of two substrates (150mm x 30mm) bonded together in an area of 100mm x 30mm, as shown in Figure 3. The experimental portion of this work consisted of the analysis of the creep rate and the peel strength in the single lap joint, subjected to tensile loading as shown in Figure 4 according to the procedures defined in EN 1392:1998 [21].

3.2.2 Creep Rate test

The creep test is performed in a heated cabinet at temperature of 60ºC. Considering the unbonded ends of the test specimen of the single lap joint, carefully fold back the more flexible material of the both adherents taking care do not to peel any of the adhesive bonds. Then use a pen to make a mark on the stiffer of the two adherents at the point of separation. Firmly clamp the free end of the more flexible adherent of a single lap joint specimen into each of moveable clamps. On each moveable clamp support is applied a mass of 1,5kg, as shown in Figure 4 a).

To obtain the results, it is necessary to open the heated cabinet over the time and mark the separations (in mm) of the bonds substrates while still loaded, to complete separation [21]. With the creep experiment it is obtained a bond failure envelope that can be divided into three phases: primary, secondary, tertiary. Primary phase correspond to an instantaneous elastic strain, secondary phase represent the creep rate and the tertiary phase happen with the failure of the bond of the specimen [9]. The primary and the tertiary phase are ignored on the calculation of the mean of the separation lengths of the bond [9, 21].

The results are expressed as displacements (mm) versus time (minutes, min). Three adhesive joint specimens for each test were considered. The heated cabinet used is a Memmert (Germany), model UM 400.

3.2.3 Peel test

The peel test is performed in the testing machine at a speed of 50 mm/min. One of the free ends of the test specimen is firmly clamp into the jaw of the tensile testing machine. As the jaw separate it is possible to observe the bond failure. The results are expressed as load (N) versus displacement (mm). The peel strength per unit of width is determined by the ratio between the maximum force and the width of the overlap joint. For each test specimen when divide the average peeling strength by the width of the specimen in millimeters, it's possible to obtain the peel strength of each bond in N/mm. Three adhesive joint specimens for each test were considered. The tensile machine used is an Instron (Norwood, MA, USA), model 3367, with load cell of 30kN, as shown in Figure 4 b).

3.3 Planning of experimental measurements

The Taguchi method [22] is adopted to plan the experimental tests (DOE) that further will be used in the ANN learning procedure. The objective of DOE is to reduce the variation in a process through robust design of experiments (DOE). The effect of many different parameters on the performance characteristic in a set of experiments can be analyzed by using orthogonal arrays. Once the parameters affecting the measuring process have been determined, the levels at which these parameters should be varied must be determined. In this work, the design of experiments are implemented using the Taguchi table $L27(3^{13})$ [7-8], [22].

4. MULTI-OBJECTIVE DESIGN OPTIMIZATION

4.1 Multi-objective based design formulation

The generic form of a multi-objective design optimization (MDO) problem can be mathematically expressed as:

$$\text{Minimize } \mathbf{f}(\mathbf{x}) = \left\{ f_i(\mathbf{x}) : \Re^n \mapsto \Re;\ i = 1,\ldots,m;\ m > 1 \right\} \text{, over } \mathbf{x}$$

subject to

$$g_j(\mathbf{x}) \geq 0;\ \left\{ g_j(\mathbf{x}) : \Re^n \mapsto \Re;\ j = 1,\ldots, p \right\} \tag{1}$$

and

$$h_k(\mathbf{x}) = 0;\ \left\{ h_k(\mathbf{x}) : \Re^n \mapsto \Re;\ k = 1,\ldots, r \right\}$$

with contradictory objectives. In the above formulation $f_i\,(i=1,\cdots,m)$ are the objective functions, the constraints $g_j(\mathbf{x})\geq 0$ and $h_k(\mathbf{x})=0$ (*j=1, …, p* and *k=1, …, r*) define the feasible space $\mathbf{Q}\subseteq\Re^n$. Usually, the corresponding minimum with respect to all objective functions is located outside $\mathbf{Q}$. There is no unique solution to a problem with more than one conflicting objectives and the existing solutions are denoted by Pareto-optimal solutions. The classification as "Pareto-optimal" depends on the concept of dominance according the following definitions [23, 24]:

<u>Definition 1</u> (dominance): Let be $\mathbf{Q}\subseteq\Re^n$ the subset in the minimization problem formulated in (1). A solution $\mathbf{x}_1\in\mathbf{Q}$ dominates a solution $\mathbf{x}_2\in\mathbf{Q}$, if the objective value for $\mathbf{x}_1$ is smaller than the objective value for $\mathbf{x}_2$ in at least one objective and is not bigger with respect to the other objectives:

$$\mathbf{x}_1 \prec \mathbf{x}_2 \Leftrightarrow \begin{cases} \forall i : 1\leq i\leq m \Rightarrow f_i(\mathbf{x}_1)\leq f_i(\mathbf{x}_2) \\ \wedge \\ \exists j : 1\leq j\leq m\ ,\ f_j(\mathbf{x}_1) < f_j(\mathbf{x}_2) \end{cases} \tag{2}$$

where $\mathbf{x}_1 \prec \mathbf{x}_2$ denotes $\mathbf{x}_1$ dominates $\mathbf{x}_2$.

<u>Definition 2</u> (Pareto optimal design): Let be $\mathbf{Q}\subseteq\Re^n$ the subset in the minimization problem formulated in (1). A solution $\mathbf{x}^*\in\mathbf{Q}$ is classified as Pareto optimal design if and only if it is not dominated by any other solution in **Q**. The set of all Pareto solutions is called the Pareto front, represented by $\mathbf{X}^*$,

$$\mathbf{x}^*\in\mathbf{X}^* \Leftrightarrow \left\{\mathbf{x}\in\mathbf{Q} :\ \mathbf{x}\prec\mathbf{x}^*\right\}=\left\{\varnothing\right\} \tag{3}$$

The above definitions are essential for further Pareto evolutionary search developments for multi-objective optimization of composite structures.

4.2 Bi-objective optimization problem of adhesive joint

The proposed approach follows the problem definition established in previous section. The multi-objective optimization (MDO) problem formulated is based on minimization of objective functions in equation (1). However, in the proposed approach the performance of structural response of the footwear adhesive joints is measured by creep rate (*CR*) and the peel strength (*PS*). In general, the optimal design of adhesive joint is performed based on minimization of creep rate and maximization of peel strength. So, this design procedure must be formatted according the formulation in equation (1). The minimization of inverse of peel strength (*1/PS*) is adopted as second objective function to overcome this apparent difficulty.

Therefore, it is intended to develop a model capable to predict and simultaneously minimize the creep rate and the inverse of peel strength depending on the weight percentage of raw materials used in the composition of the adhesive joint. These design variables denoted by vector **x** with components x_k, are the weight percentages of PUs, resins and additives in the adhesive composition. The mathematical formulation of the bi-objective optimization problem of adhesive joint is defined as creep rate and inverse of peel strength minimizations subject to technological constraints as follows,

$$\textit{Minimize}\ \left(f_1(\mathbf{x}), f_2(\mathbf{x})\right),\ \text{ over }\ \mathbf{x} \tag{4}$$

with $f_1(\mathbf{x}) = CR(\mathbf{x})$ and $f_2(\mathbf{x}) = \dfrac{1}{PS(\mathbf{x})}$

subject to:

$$10 \le \sum_{k=1}^{n} x_k \le 20 \tag{5}$$

$$\sum_{k=1}^{r} x_{n+k} \le 1 \tag{6}$$

$$\sum_{k=1}^{a} x_{r+k} \leq 7 \tag{7}$$

$$x_k^l \leq x_k \leq x_k^u \quad , \quad k = 1, \cdots, n + r + a \tag{8}$$

where *n*, *r* and *a* are the number of materials of each group of PUs, resins and additives considered for the adhesive joint, respectively. Those numbers will be defined in design process. The constants x_k^l and x_k^u are the lower and upper bounds of design variable x_k, respectively.

4.3 Stages of MDO approach

The proposed multi-objective design optimization (MDO) approach is based on mixed experimental-numerical procedures according Section 2. The strategy to build the MDO approach to solve the bi-objective optimization problem formulated from equation (4) to equation (8) is based on three columns as previously referred: 1. the construction of physical model representation; 2. the adopted multi-objective optimization algorithm; and 3. the architecture of the optimization model connecting the different modulus.

The experimental data obtained in Section 3 is essential to build the numerical model of physical phenomenon, which is the adhesive joint behavior. The numerical representation will be used in optimal design procedure. So, two stages are identified in numerical part of the proposed mixed experimental-numerical approach as shown in Figure 5. These two stages are:

1) *ANN learning procedure* where the experimental results are used to obtain the optimal ANN configuration, which supports the relationship between the weight composition of raw materials and the performance functions as creep rate and the peel strength;

2) *Optimal design procedure* where the MDO concepts are applied to search the constrained bi-objective optimization of the adhesive joint based on creep

rate minimization and peel strength maximization using the weight composition of raw materials as design variables.

The procedure of the first stage begins defining the set of planned experiments based on Taguchi method is proposed in Section 3. Then, the experimental input/output patterns are used in *learning procedure* aiming to obtain the optimal ANN configuration [17, 25]. The *ANN learning procedure* is equivalent to solve an optimization problem based on minimization of the differences between the experimental results and the simulation values obtained from the ANN. So, detailing the process the optimal configuration of ANN is obtained minimizing the error between the simulated network outputs and the experimental data for creep rate (CR) and the peel strength (*PS*). In this stage the design variables are the weights of synapses, $m_{ij}^{(p)}$, and the biases, $r_k^{(p)}$, of the ANN.

The minimization of ANN *learning procedure* is performed using a single Genetic Algorithm denoted by $\mathbf{GA}^{(1)}$ with appropriated genetic parameters. Since the GA is a population-based evolutionary method in this stage a population of solutions for ANN configuration denoted by $\mathbf{P}^{(t)}$ is considered at each *t*-generation. After the ANN learning procedure the optimal configuration denoted by $\mathbf{P}_{\mathrm{ANN}}{}^{\mathrm{opt}}$ is obtained and the construction of physical model representation is finished. This corresponds to optimal values for the weights of synapses, $m_{ij}^{(p)}$, and the biases, $r_k^{(p)}$, of the ANN.

During the *optimal design procedure*, the bi-objective optimization problem formulated from equation (4) to equation (8) is solved using the MDO concepts. The evaluation of the objective functions are based on optimal configuration $\mathbf{P}_{\mathrm{ANN}}{}^{\mathrm{opt}}$ of the ANN obtained at the first stage. The *optimal design procedure* is a multi-objective constrained minimization performed using the genetic algorithm denoted by $\mathbf{GA}^{(2)}$ with genetic parameters different from previous stage.

The trade-off between minimum creep rate and minimum inverse peel strength, depending on given size and technological constraints imposed on the weight composition of raw materials used in adhesive joint, is searched. A short population of solution, $\mathbf{X}^{(t)}$, is used to evolve through the $\mathbf{GA}^{(2)}$ based on an elitist strategy. These solutions are associated with different compositions of PUs, resins and additives for the adhesive joint.

The best solutions of $\mathbf{X}^{(t)}$ are stored into an enlarged population, $\mathbf{EP}^{(t)}$ based on dominance concepts. The global Pareto-optimal front is built at this enlarged population using the concept of Pareto dominance [24]. The enlarged population is updated and ranked every generation and the worst ranking solutions are eliminated. The search method adopts an elitist strategy storing non-dominated solutions found during the evolutionary process into the enlarged dominance-based population. After the stopping criteria are reached, it is obtained the optimum adhesive composition. Figure 5 shows the integrated ANN learning and optimal design procedures.

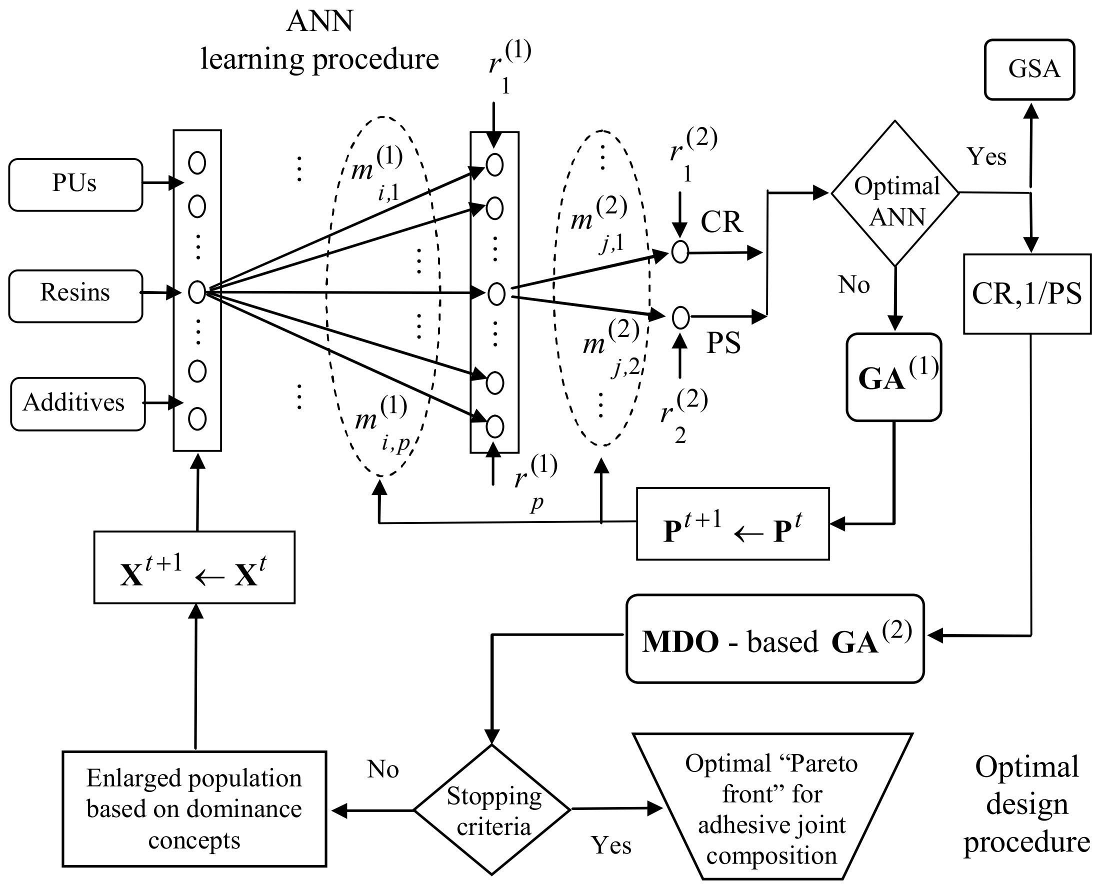


Figure 5. Integrated ANN learning and optimal design procedures.

Inside the integrated ANN learning and optimal design procedures at the end of ANN optimal configuration search a ANN-based Monte Carlo simulation procedure is implemented aiming to study the sensitivity of the structural response of adhesive joint relatively to design variables of the MDO process. This procedure is called sensitivity analysis (SA) as shown in Figure 5.

4.4 First stage: ANN learning procedure

The Artificial Neural Network (ANN) is a nonlinear dynamic modeling system inspired by our understanding and abstraction on the biological structure of the human brain. Its architecture and operating procedures are based on a large number of highly interconnected processing units denoted by neurons and the linkages are similar to the brain synapses as in biological sense. The operating procedures include attributes such as learning, thinking, memorizing, remembering, rationalizing and problem solving [25].

In the ANN development a weight value is associated with each synaptic connection between processing units that is defined as the connection importance. The weight value acts as a multiplicative filter together with the activation procedure performed by an appropriated function. The ANN architecture is formed by several layers of neurons and different matrices with synaptic weights can be identified as linkage elements between layers. Learning of ANN occurs while modification of connection weight matrix is undertaken at the learning process. From examples of a phenomenon with particular behavior and following an appropriate learning rule the ANN acquires knowledge or relationship embedded in the input/output data. The ANNs are robust models having properties of universal approximation, parallel distributed processing, learning, adaptive behaviour and can be applied to multivariate systems [17, 25].

In this work, the proposed ANN is organized into three layers of nodes (neurons): input, hidden and output layers. The synapses between input and hidden nodes and between hidden and output nodes are associated with weighted connections that establish the relationship between input data and output data. Deviations on neurons belonging to hidden and output layers are also considered in the proposed ANN model. In the developed ANN, the input data vector $\mathbf{D}^{inp}$ is defined by a set of experimental values for design/input variables $\mathbf{x}$, which are the weight composition of raw materials of the adhesive joint, such as PU's, resins and additives as referred in previous sections. The corresponding output data vector $\mathbf{D}^{out}$ contains the experimental values of the creep rate and of the peel strength.

The data vectors $\mathbf{D}^{inp}$ and $\mathbf{D}^{out}$ used to build the ANN needs to be normalized aiming to avoid numerical error propagation during the learning process. Then each component of normalized vectors are done as follows,

$$\underline{D}_k = (D_k - D_{min}) - \frac{D_N^{max} - D_N^{min}}{D_{max} - D_{min}} + D_N^{min} \tag{9}$$

where D_k is the k-th component of the vector of experimental values before normalization, D_{min} and D_{max} are the minimum and maximum values of D_k, respectively, in the input/output data set to be normalized. According to Equation (9), the data set is normalized to values $\underline{D}_k$, verifying the conditions

$$D_N^{min} \leq \underline{D}_k \leq D_N^{max} \tag{10}$$

Depending on the input or output data, different maximum and minimum normalized values are used in Equation (9).

The weights of the synapses, $m_{ij}^{(p)}$, and biases in the nodes or neurons at the hidden and output layers, $r_k^{(p)}$, are controlled during the learning procedure as shown in Figure 5. The signal in each node is $C_k^{(p)}$ defined as the components of the vector $\mathbf{C}^{(p)}$ given by

$$\mathbf{C}^{(p)} = \mathbf{M}^{(p)} \mathbf{D}^{(p)} + \mathbf{r}^{(p)} \tag{11}$$

where $\mathbf{M}^{(p)}$ is the matrix of the weights of synapses associated with the connections between input and hidden layer (*p*=1) or between hidden and output layer (*p*=2), $\mathbf{r}^{(p)}$ is the biases vector considered for the nodes of the hidden (*p*=1) or output (*p*=2) layers, $\mathbf{D}^{(p)}$ is the input data vector for the hidden (*p*=1) or output (*p*=2) layer.

The sums of the changed signals (total activation) in Equation (11) are inserted in the Activation Functions. A sigmoid function is applied on each node on hidden layer while a linear function is considered for output layer. The activation of the *k-th* node of the hidden layer (p=1) or output layer (p=2) and is obtained through sigmoid functions as follows:

$$A_k^{(1)} = \frac{1}{1+e^{-\eta\, C_k^{(1)}}} \qquad (12)$$

$$A_k^{(2)} = C_k^{(2)} \qquad (13)$$

where $A_k^{(1)}$ and $A_k^{(2)}$ represent the activation functions of the signal of the nodes or neurons of the hidden and output layers, respectively. The scaling parameters η influence the sensitivity of the sigmoid activation function and must be controlled.

The supervised learning of ANN followed in this approach is an evolutionary optimization procedure performed by $\mathbf{GA}^{(1)}$. This procedure is based on the minimization of the error between experimental output data and ANN simulated results. In the optimization process the weights of synapses and the biases in neurons are used as design variables. For each set of input data and any configuration of the weight matrices $\mathbf{M}^{(p)}$ and biases $\mathbf{r}^{(p)}$, with p=1 and p=2, a set of output results is obtained. These simulated output results are compared with the experimental output values obtained for the same input data to evaluate the difference (or error), which must be minimized during the learning procedure [25].

The supervised learning of the proposed ANN is based on several measures of the error with the objective to accelerate and stabilize the learning process. The first measure is the root-mean-squared error defined as

$$RMSE = \frac{1}{N_{exp}} \sqrt{\sum_{i=1}^{N_{exp}} \left[\left(CR_i^{sim} - CR_i^{exp} \right)^2 + \left(PS_i^{sim} - PS_i^{exp} \right)^2 \right]} \qquad (14)$$

where N_{exp} is the number of experiments considered in the set of design points of Taguchi and the superscripts *sim* and *exp* denote the simulated and experimental data of creep rate, *CR* and peel strength, *PS*. To reinforce the error minimization a second measure is introduced based on the following mean relative error component:

$$RE = \frac{1}{N_{exp}} \sqrt{\sum_{i=1}^{N_{exp}} \left[\left(\frac{CR_i^{sim} - CR_i^{exp}}{CR_i^{exp}} \right)^2 + \left(\frac{PS_i^{sim} - PS_i^{exp}}{PS_i^{exp}} \right)^2 \right]} \tag{15}$$

The influence of the biases of the neurons of the hidden and output layers is also included to stabilize the learning process:

$$\mathbf{\Gamma} = \frac{1}{N_{exp}} \sum_{i=1}^{N_{exp}} \left[\frac{1}{N_{hid}} \sum_{k=1}^{N_{hid}} \left(r_k^{(1)} \right)^2 + \frac{1}{N_{out}} \sum_{k=1}^{N_{out}} \left(r_k^{(2)} \right)^2 \right] \tag{16}$$

where N_{hid} and N_{out} are the number of neurons of the hidden layer and of the output layer, respectively.

The error measures presented from Equations (14) and (15) and biases component in Equation (16) are aggregated using the following formula:

$$F_1\left(\mathbf{M}^{(1)}, \mathbf{r}^{(1)}, \mathbf{M}^{(2)}, \mathbf{r}^{(2)}\right) = c_1\, RMSE + c_2\, RE + c_3\, \mathbf{\Gamma} \tag{17}$$

being the constants c_k used to regularize the numerical differences of the three error terms stabilizing the numerical procedure. The weights of the synapses and biases can be changed until the value of F_1 falls within a prescribed value.

The adopted supervised learning process of the ANN is based on a Genetic Algorithm denoted by $\mathbf{GA}^{(1)}$ [26-28] using the weights of synapses $\mathbf{M}^{(p)}$, and biases of neural nodes at the hidden and output layers $\mathbf{r}^{(p)}$, as design variables as shown in Figure 5. At this stage a population of solutions for ANN configuration denoted by $\mathbf{P}^{(t)}$ is considered at each *t*-generation.

A binary code format is used for these variables. The number of digits of each variable can be different depending on the connection between the input-hidden layers or hidden-output layers. The domain of the learning variables $\mathbf{M}^{(p)}$ and $\mathbf{r}^{(p)}$ (p=1 and p=2) and scaling parameter η can be tuning together the code format of design variables of the ANN learning procedure. The optimization problem formulation associated with the ANN learning process is based on the minimization of the function defined in Equation (17) without constraints, as follows

Maximize $FIT^{(1)} = K^{(1)} - F_1\left(\mathbf{M}^{(1)}, \mathbf{r}^{(1)}, \mathbf{M}^{(2)}, \mathbf{r}^{(2)}\right)$ over $\mathbf{M}^{(p)}$ and $\mathbf{r}^{(p)}$ (18)

subject to $\mathbf{M}^{(p)}, \mathbf{r}^{(p)} \in \mathbf{\Omega}$ (p=1 and p=2),

where $\mathbf{\Omega}$ is the domain of design variables in learning procedure, $FIT^{(1)}$ is the fitness function in GA search to obtain the optimal ANN configuration, $\mathbf{P}_{\mathrm{ANN}}{}^{\mathrm{opt}}$ for the weight of synapses and biases in neurons. Since the selection operator of GA is fitness-based the function $FIT^{(1)}$ must take positive values. So, the constant $K^{(1)}$ must be large enough to obtain always positive fitness values.

The single Genetic Algorithm $\mathbf{GA}^{(1)}$ used to solve the constrained optimization problem (with size constraints) defined in Equation (18) performs in following sequence:

- Step1: *Initialization* of population $\mathbf{P}^{(0)}$. The initial population of design solutions for the learning variables $\mathbf{M}^{(p)}$ and $\mathbf{r}^{(p)}$ (p=1 and p=2) is randomly generated using a uniform probability distribution function (PDF).
- Step 2: *Mating selection mechanism*. The population $\mathbf{P}^{(t)}$ is ranked according to individual fitness obtained using the formulae defined from Equation (15) to Equation (18). The best-fitted elite group of $\mathbf{P}^{(t)}$ is determined. One couple of parents p_1 and p_2 per each offspring individual is generated. The procedure is elitist: one from the best-fitted group (elite) and another from the least fitted one.
- Step 3: *Offspring generation mechanism*. The crossover operator generates a new chromosome (offspring) by recombination of the genetic material of each couple of parent chromosomes p_1 and p_2. The

offspring genetic material is obtained using the multi-point combination technique known as *parameterized uniform crossover* [27-28]. This crossover operator is applied with a predefined probability to select the offspring genetic material from the best-fitted chromosome. The offspring generation mechanism is repeated until the offspring group $\mathbf{B}^{(t)}$ is completed.

- Step 4: *Intermediate selection*. The current population $\mathbf{P}^{(t)}$ is transferred to an intermediate stage where is joined to the offspring group $\mathbf{B}^{(t)}$ generating the enlarged population $\mathbf{P}^{(t)} \cup \mathbf{B}^{(t)}$.
- Step 5: *Elimination/Replacement* by genetic similarity control. The enlarged population $\mathbf{P}^{(t)} \cup \mathbf{B}^{(t)}$ is ranked according to the individual fitness. Then, the similarity control is performed gene by gene following an updating scheme during the evolutionary process. The objective is to control the population diversity keeping it in good level and reducing the endogamy properties of Crossover operator. This is followed by elimination of solutions with similar genetic properties and subsequent replacement by new randomly generated individuals. The new population $\mathbf{P}^{(t+1,*)}$ is ranked and the individuals with worst fitness are replaced by a group of new solutions obtained from the Mutation operator. During this procedure the original size of the population is recovered.
- Step 6: *Mutation*. In the presented approach the mutation genetic operator is used to overcome the problem induced by selection and crossover operators where can happen some generated solutions have a large percentage of equal genetic material. So, aiming to improve the diversity level a chromosome set group which genes are generated in a random way is introduced into the population. Since this new group of chromosomes will be recombined with the remaining individuals into the population during next generations this operation is called *Implicit Mutation* [26].
- Step 7: *Final selection*. After mutation, the new population $\mathbf{P}^{(t+1)}$ is obtained and the evolutionary process will continue until the stopping criteria are reached.

- Step 8: *Stopping cri*terion analysis. The stopping criterion used in the convergence analysis is based on the relative variation of the mean fitness of a reference group inside $\mathbf{P}^{(t+1)}$. The search is stopped if the mean fitness of the reference group does not evolve after a finite number of generations. Otherwise, the population evolves to the next generation returning to Step 2.

4.5 Second stage: optimal design procedure

The *optimal design procedure* is based on MDO concepts applied to solve the bi-objective constrained minimization problem formulated from Equation (4) to Equation (8). The objectives to be minimized are the creep rate and the inverse of peel strength subject to technological constraints associated to the weight percentages of raw materials used in the composition of the adhesive joint. These design variables denoted by vector **x** with components x_k, are the weight percentages of PUs, resins and additives in the adhesive composition.

The fitness assignment is based on an aggregation function of the two objectives $f_1(\mathbf{x}) = CR(\mathbf{x})$ and $f_2(\mathbf{x}) = \dfrac{1}{PS(\mathbf{x})}$, and a graded penalization of constraint violation [26-27]. So, the original bi-objective optimization problem is transformed as follows:

$$Maximize \;\; FIT^{(2)} = K^{(2)} - \alpha_1 f_1(\mathbf{x}) - \alpha_2 f_2(\mathbf{x}) - \alpha_3 \sum_{i=1}^{N_g} \mathbf{\Phi}_i(\mathbf{x}) \;, \quad \text{over } \mathbf{x} \tag{19}$$

$$\text{with} \qquad \mathbf{\Phi}_i(\mathbf{x}) = \begin{cases} 0 & , \quad \text{if } \varphi_i(\mathbf{x}) \le 0 \\ R_i \left| \varphi_i(\mathbf{x}) \right|^{q_i} & , \quad \text{if } \varphi_i(\mathbf{x}) > 0 \end{cases} \tag{20}$$

where $\varphi_i(\mathbf{x})$ are the constraints defined from Equation (5) to Equation (7) after normalization. Here, $\varphi_i(\mathbf{x}) \le 0$ are associated to the feasibility of the constraint

$\varphi_i(\mathbf{x})$. The N_g constraints defined from Equation (5) to Equation (7) must be normalized relatively to their bound limits aiming to avoid scaling effects. Unfeasible solutions of the problem are penalized depending on the total magnitude of the constraints violation. Furthermore, the penalization is applied on the graded degree of severity according to the difference between the current and the allowable constraint values. The constants q_i and R_i are evaluated considering two constraint violation degrees, i.e., strong penalization for large violation value and fair penalization for negligible violation of the constraints [26-28]. The constants α_i are introduced for numerical regularization. Since the stochastic permutation of data in genetic search is performed using fitness-based selection procedures the fitness function $FIT^{(2)}$ must be positive. So, the constant $K^{(2)}$ is large enough to obtain always positive fitness values. The size constraints in Equation (8) are not included in described procedure of penalization. They are imposed directly to the design space at the binary code format transformation used on genetic algorithm development.

The MDO process evolution is based on a short population of solutions $\mathbf{X}^{(t)}$ updated during the evolutionary search driven by the genetic algorithm, $\mathbf{GA}^{(2)}$. An elitist strategy is adopted at evolution of $\mathbf{X}^{(t)}$. Each solution in $\mathbf{X}^{(t)}$ is ranked according its fitness value, which is related with the objective functions and the constraints of the problem. The trade-off between minimum creep rate and minimum inverse peel strength, depending on given size and technological constraints imposed on the weight composition of raw materials used in adhesive joint, is searched.

From Equation (19) and (20) it can be established that designs with good fitness and satisfying the constraints have priority in the rank process. Although this is necessary for bi-objective optimization problem it is not essential to build the optimal Pareto front. Indeed, the Pareto front depends on the dominance concept, which is applied at enlarged population. Here, the short population $\mathbf{X}^{(t)}$ is used as a nest where the good solutions are generated through the

$\mathbf{GA}^{(2)}$ based on an elitist strategy. At each generation the best solutions of $\mathbf{X}^{(t)}$ are stored into an enlarged population, $\mathbf{EP}^{(t)}$ based on dominance concepts. The global Pareto-optimal front is built at this enlarged population using the concept of Pareto dominance [24].

Inside the enlarged population defined here as set $\mathbf{EP}^{(t)} \subseteq \Re^n$, individuals are sorted and ranked according to non-constrain-dominance. Following the definition by Deb [23], an individual $\mathbf{x}_i \in \mathbf{EP}^{(t)}$ is said to constrain-dominate an individual $\mathbf{x}_j \in \mathbf{EP}^{(t)}$, if any of the following conditions are verified:

(1) $\mathbf{x}_i$ and $\mathbf{x}_j$ are feasible, with

(i) $\mathbf{x}_i$ is no worse than $\mathbf{x}_j$ for all objectives, and

(ii) $\mathbf{x}_i$ is strictly better than $\mathbf{x}_j$ in at least one objective,

(2) $\mathbf{x}_i$ is feasible while individual $\mathbf{x}_j$ is not,

(3) $\mathbf{x}_i$ and $\mathbf{x}_j$ are both infeasible, but $\mathbf{x}_i$ has smaller total constraint violation.

The constraint violation of an individual $\mathbf{x}$ is defined to be equal to the sum of the violated constraint function values in the multi-objective optimization problem formulated from (4) to (8) [24]:

$$\xi(\mathbf{x}) = \sum_{i=1}^{N_g} \mathbf{\Gamma}_i(\mathbf{x}) \tag{21}$$

where $\mathbf{\Gamma}_i(\mathbf{x}) = \mathbf{\Gamma}_i[\varphi_i(\mathbf{x})]$, with

$$\mathbf{\Gamma}_i[\varphi_i(\mathbf{x})] = \begin{cases} 0 & \text{if} \quad \varphi_i(\mathbf{x}) \le 0 \\ \varphi_i(\mathbf{x}) & \text{if} \quad \varphi_i(\mathbf{x}) > 0 \end{cases} \tag{22}$$

where $\varphi_i(\mathbf{x})$ are the constraints defined from Equation (5) to Equation (7) after normalization. The concept of constrain-domination enables to compare two individuals in problems having multiple objectives and constraints, since if $\mathbf{x}_i$ constrain-dominates $\mathbf{x}_j$, then $\mathbf{x}_i$ is better than $\mathbf{x}_j$. If none of the three conditions referred above are verified, then $\mathbf{x}_i$ does not constrain-dominate $\mathbf{x}_j$.

The Genetic Algorithm $\mathbf{GA}^{(2)}$ is used to solve the bi-objective constrained optimization problem defined from Equation (4) and Equation (8) and performs in following sequence [24, 26-28]:

- Step1: *Initialization of the short population* $\mathbf{X}^{(0)}$. The initial population of design solutions for $\mathbf{x}$ is randomly generated using a uniform probability distribution function (PDF).
- Step 2: *Mating selection mechanism*. The short population $\mathbf{X}^{(t)}$ is ranked according to individual fitness defined in Equation (19) and Equation (20). The elite group of $\mathbf{X}^{(t)}$ is determined. One couple of parents $\mathbf{z}_1$ and $\mathbf{z}_2$ per each offspring individual is generated. The mating selection is elitist: one parent comes from the elite group and another from the least fitted one.
- Step 3: *Offspring generation mechanism*. The crossover operator generates a new offspring chromosome by recombination of the genes of each couple of parent chromosomes $\mathbf{z}_1$ and $\mathbf{z}_2$. The offspring genetic material is obtained using the multi-point combination technique known as *parameterized uniform crossover* [26-27]. This crossover operator is applied with a predefined probability to select the offspring genetic material from the best-fitted chromosome. The procedure is repeated until the offspring group $\mathbf{O}^{(t)}$ is completed.
- Step 4: *Intermediate selection*. The current short population $\mathbf{X}^{(t)}$ is transferred to an intermediate stage where is joined to the offspring group $\mathbf{O}^{(t)}$ generating the intermediate short population $\mathbf{X}^{(t)} \cup \mathbf{O}^{(t)}$.

- Step 5: *Elimination/Replacement* by genetic similarity control. The population $\mathbf{X}^{(t)} \cup \mathbf{O}^{(t)}$ is ranked according to the individual fitness. Then, the similarity control is performed gene by gene followed by elimination of solutions with similar genetic properties and subsequent replacement by new randomly generated individuals. The new short population $\mathbf{X}^{(t+1,*)}$ is ranked and the individuals with worst fitness are replaced by a group of new solutions obtained from the Mutation operator. During this procedure the original size of the short population is recovered.
- Step 6: *Implicit Mutation*. A chromosome set group which genes are generated in a random way is introduced into the population. This new group of chromosomes will be recombined with the remaining individuals into the population during next generations [26, 27]. After mutation, the new short population $\mathbf{X}^{(t+1)}$ is obtained.
- Step 7: *Building of global Pareto front*. At the beginning (*t*=0), all individuals of short population, $\mathbf{X}^{(t+1)}$ are transferred to enlarged population, $\mathbf{EP}^{(t)}$. At each generation, for *t*>0, the individuals generated by "new" inside $\mathbf{X}^{(t+1)}$ are transferred to $\mathbf{EP}^{(t)}$. A genetic similarity control is performed at $\mathbf{EP}^{(t)}$. The $\mathbf{EP}^{(t)}$ is organized based on the concept of dominance applied in each *t*-th generation of the evolutionary process [24]. To do this the concepts of dominance previously described are applied to individuals stored at $\mathbf{EP}^{(t)}$. Given the size and history of this population, the dominance is applied in the global sense, allowing the progressive construction of global Pareto front. As the process is continuously applied at every generation, it is possible that an individual with non-dominated status will be subsequently dominated. After some generations the individual solution $\mathbf{x}_i \in \mathbf{EP}^{(t)}$ is eliminated if $rank(\mathbf{x}_i) \geq \bar{r}$, where $\bar{r}$ is the maximum ranking of $\mathbf{EP}^{(t)}$. This leads to an increased historical record of global rank 1 individuals / non-dominated solutions inside $\mathbf{EP}^{(t)}$ during the course of the evolutionary process obtaining finally the global Pareto front [24]. The enlarged population $\mathbf{EP}^{(t)}$ is continuously updated during the evolutionary process.

- Step 8: *Final selection*. The new short population $\mathbf{X}^{(t+1)}$ is transferred to next generation and the evolutionary process will continue until the stopping criteria are reached.
- Step 9: *Stopping criterion* analysis. The stopping criterion used in the convergence analysis is based on the relative variation of the mean fitness of a reference group inside short population $\mathbf{X}^{(t+1)}$ considering the constraints feasibility. The search is stopped if the mean fitness of the reference group does not evolve after a finite number of generations. Otherwise, the short population, $\mathbf{X}^{(t+1)}$ evolves to the next generation returning to Step 2. If the convergence is reached then the optimal Pareto front (rank 1) is found inside enlarged population $\mathbf{EP}^{(t)}$ (rank 1 solutions).

5. GLOBAL SENSITIVITY ANALYSIS

The study of the influence of the weight composition of raw materials on the structural response of adhesive joint is performed based on the Global Sensitivity Analysis (GSA) supported by variance-based methods [18, 19, 29-31]. The creep rate, *CR* and the peel strength, *PS* are considered as measures of structural response of the adhesive joint. On other words, the objective is to measure and to rank the importance of the variability of design variables - the weight percentages of PUs, resins and additives in the adhesive composition, on the structural response of adhesive joint measured by creep rate, *CR* and the peel strength, *PS*.

Lets consider β_j the response functional, denoting the creep rate or the peel strength. Assuming that the variables are independent, the variance of the conditional expectation $var(E\langle\beta_j \mid x_i\rangle)$ is used as an indicator of the importance of the design variable x_i on the variance of β_j. This indicator is directly proportional to the importance of x_i. In particular, the first-order global sensitivity index of Sobol [18, 19, 29-31] is used as normalized indicator:

$$S_i(\beta_j) = \frac{var\left(E\langle \beta_j \mid x_i \rangle\right)}{var(\beta_j)} \qquad (23)$$

In this work, the above first-order global sensitivity index of Sobol is calculated using the Monte Carlo simulations method together Artificial Neural Network (ANN). So, the GSA is implemented using the optimal network configuration $\mathbf{P}_{\text{ANN}}{}^{\text{opt}}$ obtained at the end of first stage: ANN learning procedure of the proposed approach. Thus, is possible to avoid the exhaustive and costly experimental tests to obtain the variability of the input variables structural on response.

The methodology to obtain the first-order global sensitivity index of Sobol is based on the algorithm proposed by António and Hofbauer [19, 31], which is described as follows:

- 1st Step: Lets consider the non-correlated design variables vector **x** following a uniform probability distribution function $Unif(0,1)$.
- 2nd Step: Considers a set of random numbers $\boldsymbol{\lambda}_{fix}$ following a uniform probability distribution function $Unif(0,1)$. These N_f random numbers are used to generate the fixed values for the design variable x_i.
- 3rd Step: For each design variable x_i (not for itself) a sample matrix $\mathbf{J}_\alpha$ is generated by independently collecting samples of (*p*-1) random numbers following a uniform distribution $Unif(0,1)$, where the size of the sample is N_r.
- 4th Step: For each design variable x_i a combination of values of $\boldsymbol{\lambda}_{fix}$ and $\mathbf{J}_\alpha$ is defined. The structural response of β_j is evaluated for **x** using the optimal configuration of the artificial neural network, $\mathbf{P}_{\text{ANN}}{}^{\text{opt}}$. The conditional expectation of structural response of adhesive joint is estimated and the mean values of this conditional expectation are

calculated. Finally, the variance of the conditional expectation of structural response fixing each design variable x_i is estimated. The procedure is repeated for all design variables.

- 5th Step: The variance of structural response $var(\beta_j)$, is estimated considering the previous simulations.
- 6th Step: Calculation of the global Sobol sensitivity index using Equation (23) for all design variables.

6. RESULTS, ANALYSIS AND VALIDATION

6.1 Planned experimental testing and results

According to the first column of the proposed optimization strategy it id needed to built physical model representing the adhesive joint of footwear product and the relationship between the design variables – the weight composition of raw materials, and the inherent structural response measured by creep rate and peel strength. Then, these testing results are used the ANN learning procedure aiming to develop the approximation model.

Several compositions of raw materials are considered in the proposed planned tests, as shown in Table 2. The design points used to plan the experiments are considered as input values in the ANN learning procedure. A number of training data sets are selected inside the interval domain of each design (random) variable and levels defined in Table 2. The Taguchi values are selected according to the approach proposed by Taguchi and Konishi [22].

Table 2. Materials used in adhesive joint and Taguchi levels definition.

	Raw-Materials	% weight on formula	Levels	Real value
PU's	1. Caprolactone with extremely high crystallization	0-20	1/2/3	2.5/5/10
	2. Polyester with extremely high crystallization	0-20	1/2/3	2.5/5/10
	3. Polyester with very high crystallization	0-20	1/2/3	2.5/5/10
Resin's	4. Colophony WW	0-1	1/2/3	0/0.2/0.5
	5. Hydrocarbon (C9)	0-1	1/2/3	0/0.2/0.5
	6. Alkyl phenolic	0-1	1/2/3	0/0.2/0.5
	7. Terpene phenolic	0-1	1/2/3	0/0.2/0.5
	8. Coumarone-Indene	0-1	1/2/3	0/0.2/0.5
	9. Vinyl Chloride / Acetate Vinyl	0-1	1/2/3	0/0.2/0.5
Additive	10. Fumaric Acid	0-0.6	1/2/3	0/0.3/0.6
	11. Hydrophobic silica	0-2	1/2/3	0/1/2
	12. Nitrocellulose	0-2	1/2/3	0/1/2
	13. Chlorinated rubber	0-3	1/2/3	0/1.5/3

Table 3. Constraints considered in adhesive joint optimization definition.

Constraints	% weight on formula
Total % PU	10-20
Total % Resins	0-1
Total % Additives	0-7

A number of 13 raw materials are considered in adhesive joint with variable weight percentage. The raw materials are grouped into polyurethanes (PUs), resins (REs) and additives (ADs). Some constraints are imposed to the three groups as presented in Table 3. These constraints are associated with some technological acknowledge on adhesive joins used in footwear industry.

Using the Taguchi Table L27(3^{13}) [22] the actual composition for each design point is obtained, as shown in Table 4. The values presented in Table 4 and Table 5, are used as input/output patterns for learning procedure of ANN.

From a first analysis of Tables 4 and Table 5 it is possible to see that maximizing the amount of colophony and hydrocarbon resin on the adhesive formulation, a very high creep rate is obtained. On other hand, maximizing the amount of resins and additives and minimizing the amount of polyurethane on the adhesive formulation, we obtain very low peel strength. These features show the needs to implement a MDO procedure.

Table 4. Taguchi design points: % weight on formulation (design variables values).

Design point	Material number												
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**
1	2.5	2.5	2.5	0	0	0	0	0	0	0	0	0	0
2	2.5	2.5	2.5	0	0.2	0.2	0.2	0.2	0.2	0.3	1	1	1.5
3	2.5	2.5	2.5	0	0.5	0.5	0.5	0.5	0.5	0.6	2	2	3
4	2.5	5	5	0.2	0	0	0	0.2	0.2	0.3	2	2	3
5	2.5	5	5	0.2	0.2	0.2	0.2	0.5	0.5	0.6	0	0	0
6	2.5	5	5	0.2	0.5	0.5	0.5	0	0	0	1	1	1.5
7	2.5	10	10	0.5	0	0	0	0.5	0.5	0.6	1	1	1.5
8	2.5	10	10	0.5	0.2	0.2	0.2	0	0	0	2	2	3
9	2.5	10	10	0.5	0.5	0.5	0.5	0.2	0.2	0.3	0	0	0
10	5	2.5	5	0.5	0	0.2	0.5	0	0.2	0.6	0	1	3
11	5	2.5	5	0.5	0.2	0.5	0	0.2	0.5	0	1	2	0
12	5	2.5	5	0.5	0.5	0	0.2	0.5	0	0.3	2	0	1.5
13	5	5	10	0	0	0.2	0.5	0.2	0.5	0	2	0	1.5
14	5	5	10	0	0.2	0.5	0	0.5	0	0.3	0	1	3
15	5	5	10	0	0.5	0	0.2	0	0.2	0.6	1	2	0
16	5	10	2.5	0.2	0	0.2	0.5	0.5	0	0.3	1	2	0
17	5	10	2.5	0.2	0.2	0.5	0	0	0.2	0.6	2	0	1.5
18	5	10	2.5	0.2	0.5	0	0.2	0.2	0.5	0	0	1	3
19	10	2.5	10	0.2	0	0.5	0.2	0	0.5	0.3	0	2	1.5
20	10	2.5	10	0.2	0.2	0	0.5	0.2	0	0.6	1	0	3
21	10	2.5	10	0.2	0.5	0.2	0	0.5	0.2	0	2	1	0
22	10	5	2.5	0.5	0	0.5	0.2	0.2	0	0.6	2	1	0
23	10	5	2.5	0.5	0.2	0	0.5	0.5	0.2	0	0	2	1.5
24	10	5	2.5	0.5	0.5	0.2	0	0	0.5	0.3	1	0	3
25	10	10	5	0	0	0.5	0.2	0.5	0.2	0	1	0	3
26	10	10	5	0	0.2	0	0.5	0	0.5	0.3	2	1	0
27	10	10	5	0	0.5	0.2	0	0.2	0	0.6	1	2	1.5

Table 5. Peel strength [N/mm] and Creep rate [mm/min] for Taguchi design points obtained by experiments.

Design point	Peel strength	Creep rate	Design point	Peel strength	Creep rate
1	4.128	0.084	**15**	7.588	0.057
2	2.356	0.155	**16**	7.183	0.035
3	0.283	0.700	**17**	7.662	0.025
4	8.924	0.134	**18**	7.134	0.018
5	5.24	0.155	**19**	7.911	0.020
6	4.791	0.097	**20**	7.414	0.029
7	7.437	0.633	**21**	7.858	0.029
8	8.284	0.043	**22**	7.769	0.095
9	7.959	0.085	**23**	5.478	0.106
10	5.514	0.159	**24**	7.724	0.058
11	7.411	0.078	**25**	4.778	0.022
12	2.313	0.334	**26**	6.558	0.031
13	7.596	0.057	**27**	7.119	0.119
14	3.879	0.144			

6.2 First stage: results and analysis of ANN learning procedure

As previously established a number of 13 raw materials are considered as input parameters against 2 output parameters, the creep rate *CR* and the peel strength, *PS*. A number of 8 neurons are considered for the hidden layer of the ANN topology. The *ANN learning procedure* described in Section 4.4 is applied in the ANN developments. The procedure is based on the solution of the maximization problem of fitness function $FIT^{(1)}$ with size constraints that is defined in Equation (18). The *ANN learning procedure* is performed by $\mathbf{GA}^{(1)}$ using a population $\mathbf{P}^{(t)}$ with 30 individuals in evolutionary search. The population $\mathbf{P}^{(t)}$ is composed by 10 and 3 individuals/solutions in elite and mutation groups, respectively [26-28]. The binary code format with five digits is adopted for weights of synapses and biases of neural nodes. The domain of learning design variables $\mathbf{\Omega}$ is associated with the intervals $[-3,3]$ and $[-2,2]$ for both input-hidden and hidden-output linkages, respectively. After 30.000 generations the *ANN learning procedure* is concluded. The constants in Equation (18) are $c_1 = 5000$, $c_2 = 1000$, $c_3 = 0$ and $K^{(1)} = 5.\times 10^5$.

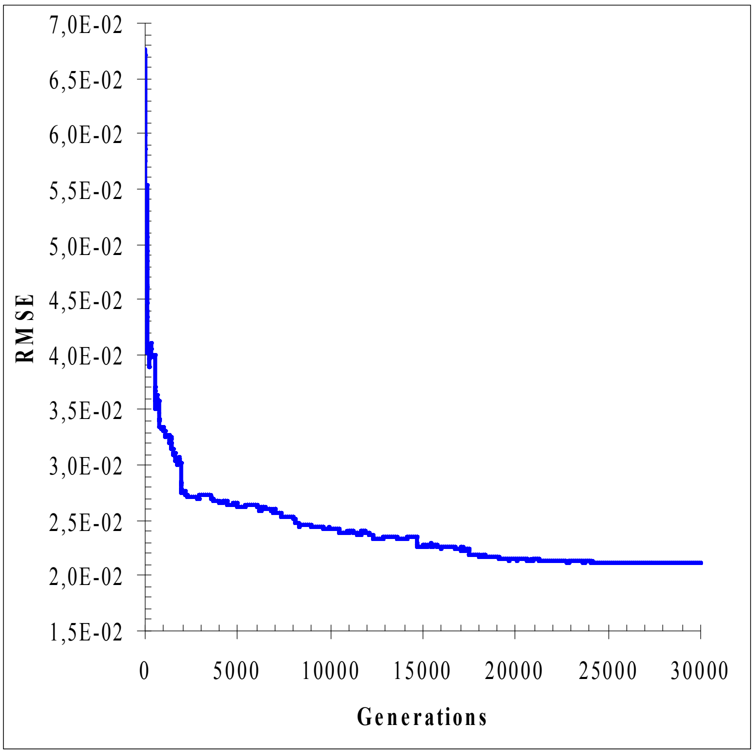


Figure 6. Evolution of root-mean squared error at *ANN learning procedure* based on GA [(1)].

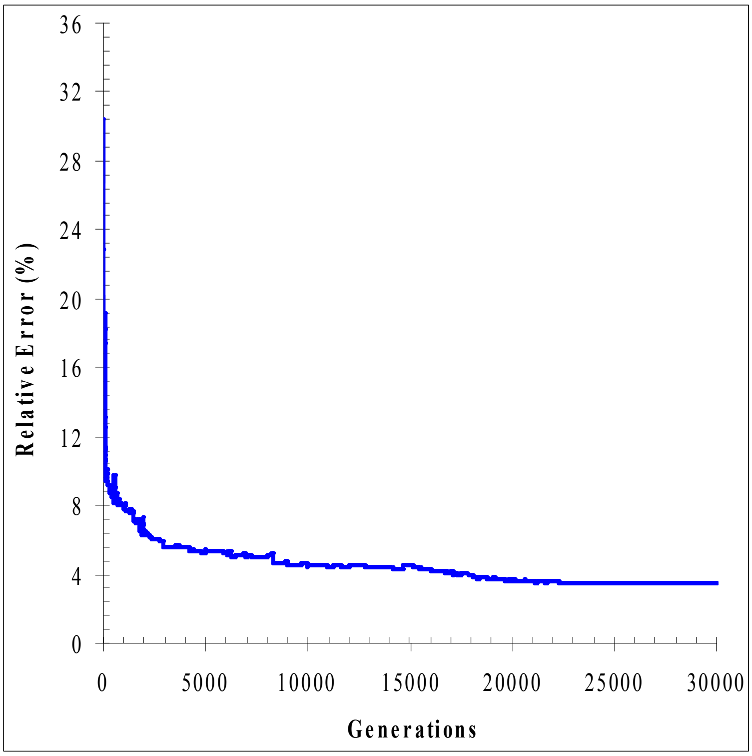


Figure 7. Evolution of mean relative error at *ANN learning procedure* based on GA [(1)].

Figures 6 and 7 show the evolution of the error parcels at *ANN learning procedure* based on $\mathbf{GA}^{(1)}$ along first stage of the proposed optimization strategy. The root-mean-squared error (RMSE) mean relative error (RE) components are defined in Equation (14) and Equation (15), respectively. The mean relative error of 3.45% is reached for optimal configuration $\mathbf{P}_{\mathrm{ANN}}{}^{\mathrm{opt}}$ at the end of *ANN learning procedure*.

6.3 Second stage: results and analysis of the optimal design procedure

The objectives to be minimized are the creep rate, C*R* and the inverse of peel strength, 1/PS (equivalent to maximize PS) subject to technological constraints associated to the weight composition of raw materials used in the adhesive joint. The design variables are the weight percentages of PUs, resins and additives in the adhesive composition. The bi-objective optimization was formulated from Equation (4) to Equation (8).

In the second stage the original constrained bi-objective optimization problem is transformed for evolutionary search format in Equation (19) and Equation (20). The MDO process evolution is based on a short population of solutions $\mathbf{X}^{(t)}$ updated during the evolutionary search driven by the genetic algorithm, $\mathbf{GA}^{(2)}$ and supported by an elitist strategy as explained in Section 4.5. Furthermore the global Pareto-optimal front is built along the evolutionary process at enlarged population, $\mathbf{EP}^{(t)}$ using the concepts of Pareto dominance detailed in Section 4.1 and Section 4.5. The fitness function $FIT^{(2)}$, depends on design variables associated with the weight percentages of raw material constituents used in the adhesive formulation. The fitness evaluation is based on optimal configuration $\mathbf{P}_{\mathrm{ANN}}{}^{\mathrm{opt}}$ of the end of first stage of *ANN learning procedure* of the proposed MDO strategy approach as shown in Figure 5.

The bi-objective optimization problem is solved with imposition of technological constraints defined from Equation (5) to Equation (7). The constraints in those equations are normalized as previously referred in Section 4.5. The constants

q_i and R_i in constraint terms on Equation (19) and Equation (20) are calculated considering two constraint violation degrees, as follows:

- a penalization equal to 100 for strong violation value equal to 0.1;
- a penalization equal to 1 for fair violation value equal to 0.01 .

The constants $\alpha_1 = \alpha_2 = 0.5$, $\alpha_3 = 1.$ and $K^{(2)} = 1.\times 10^4$ are select for fitness function $FIT^{(2)}$ defined in Equation (19).

A short population $\mathbf{X}^{(t)}$ with 30 individuals is considered on the evolutionary search performed by $\mathbf{GA}^{(2)}$. The elite and mutation groups used in $\mathbf{GA}^{(2)}$ have 10 and 6 solutions, respectively [26-28]. The side constraints in Equation (8) associated with upper and lower limits for design variables – the weight composition of raw materials are according to the third column of Table 2. The design variables are encoded using a binary code format with 5 digits. A number of 8000 generations is considered in MDO evolutionary search performed by $\mathbf{GA}^{(2)}$ on to this second stage of the proposed optimization strategy approach.

Figure 8 shows the distribution of solutions at two moments of evolution of the enlarged population, $\mathbf{EP}^{(t)}$, namely for *t*=2000 generations and *t*=8000 generations. The concepts of Pareto dominance are applied to individuals stored in $\mathbf{EP}^{(t)}$. After some generations the individual solution $\mathbf{x}_i \in \mathbf{EP}^{(t)}$ is eliminated if $rank(\mathbf{x}_i) \geq \bar{r}$, where $\bar{r} = 20$ is the maximum ranking of $\mathbf{EP}^{(t)}$ as established in Section 4.5. An improvement is observed from generation *t*=2000 to generation *t*=8000 in ranked solutions. The minimization of both objectives drives the ranked solutions toward the left and lower corner of the graph.

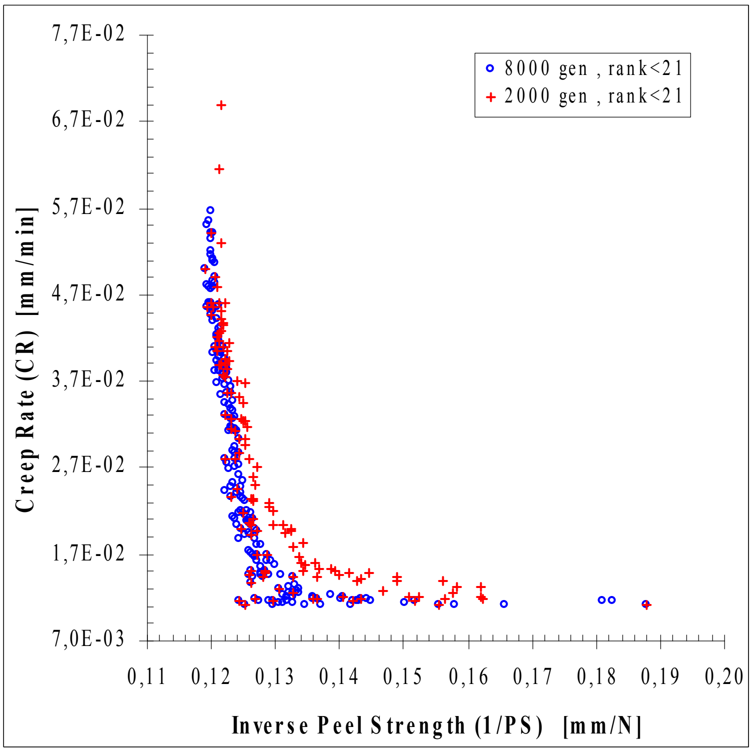


Figure 8. Evolution of solutions (rank<21) for the constrained bi-objective optimization.

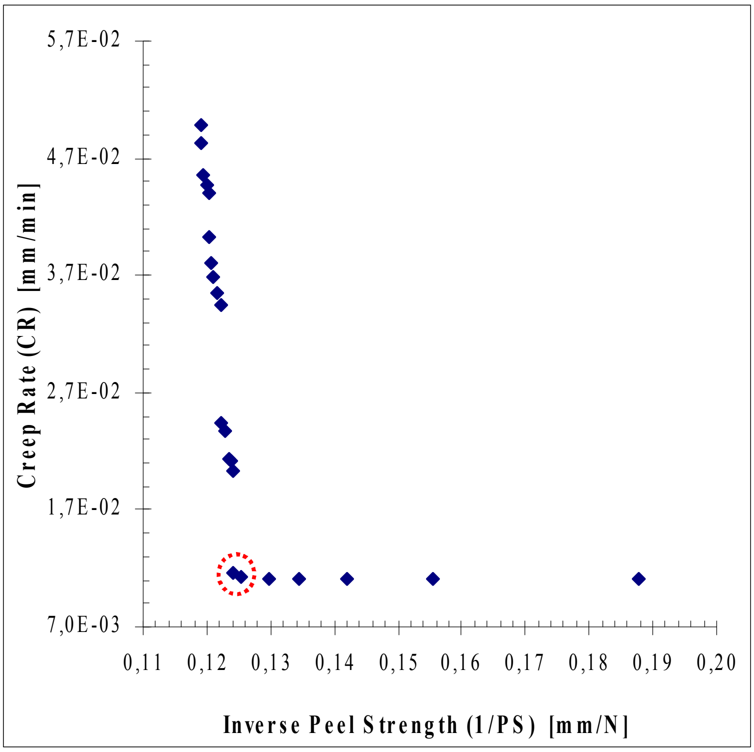


Figure 9. Optimal Pareto front (8000 generations) for the constrained bi-objective optimization procedure with possible best trade-off solutions (dashed line circle).

At the end of the optimization process, the Pareto front representing the frontier of the trade-off between the minimum creep rate and minimum inverse peel strength (maximum peel strength) for footwear adhesive joints is obtained, as shown in Figure 9. The global dominance measured in enlarged population $\mathbf{EP}^{(t)}$ at end of optimal design procedure is used to trace the associated Pareto front. The performance of the proposed approach to search for Pareto front's solutions considering the MDO problem can be observed.

According to the considerations made in Section 4.3, the point on the optimal Pareto front associated with the minimum distance to origin (utopia point) can be defined as the best mathematical trade-off between the minimum creep rate and minimum inverse peel strength (maximum peel strength). Two points are identified by dashed line circle in Figure 9. Their values of the objective functions of the bi-objective optimization problem and the corresponding optimal best trade-off solutions for the weight composition of raw material of the adhesive joint are presented in Figure 10. The design variables are numbered according Table 2.

Table 6. Feasibility of composition group values for the two best trade-off solutions.

Composition of adhesive joint	Constraints % weight	CR=0.011198 [mm/min], PS=7.985 [N/mm] % weight	CR=0.011567 [mm/min], PS=8.052 [N/mm] % weight,
Total % PU	10-20	19.355	17.903
Total % Resins	0-1	0.952	0.935
Total % Additives	0-7	4.729	3.419

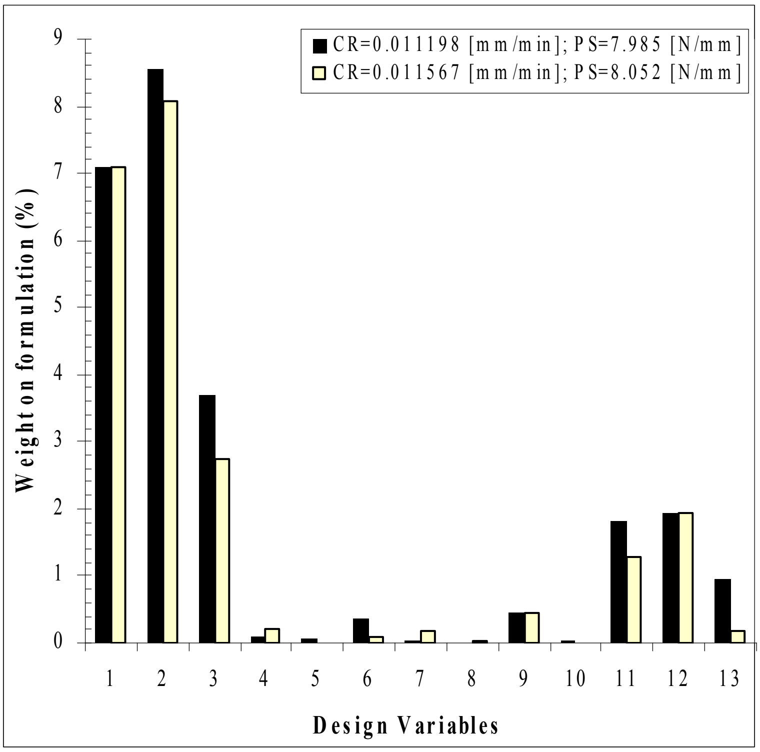


Figure 10. Compositions of the adhesive joint for two best trade-off solutions collected from the optimal Pareto front.

The optimal values shown in Figure 10 are obtained under constraints on weight composition of raw materials of the adhesive joint as referred in Table 3. The feasibility of composition group values for the two trade-off solutions can be observed by comparison with constraint intervals presented in Table 6.

The optimal results corresponding to the two best trade-off solutions of the constrained bi-objective optimization problem solved using the proposed approach is consistent with the experimental testing data used to implement the model. Indeed, the creep rate and the inverse of peel strength are minimized when large quantities for PUs (design variables 1-3) and for some quantities of additives (design variables 10-13) are considered. In this case the resins` group is not important except the weight percentage of Vynil (design variable 9).

6.4 Experimental validation of results

Experimental tests are implemented using the optimal design values presented in previous section. In particular, the best trade-off Pareto front solution corresponding to numerical values CR=0.011198 [mm/min], PS=7.985 [N/mm] shown in Figure 10, is used for experimental validation. The weight formulation (%) of raw materials of the solution is considered to build the test pieces for the experimental validation.

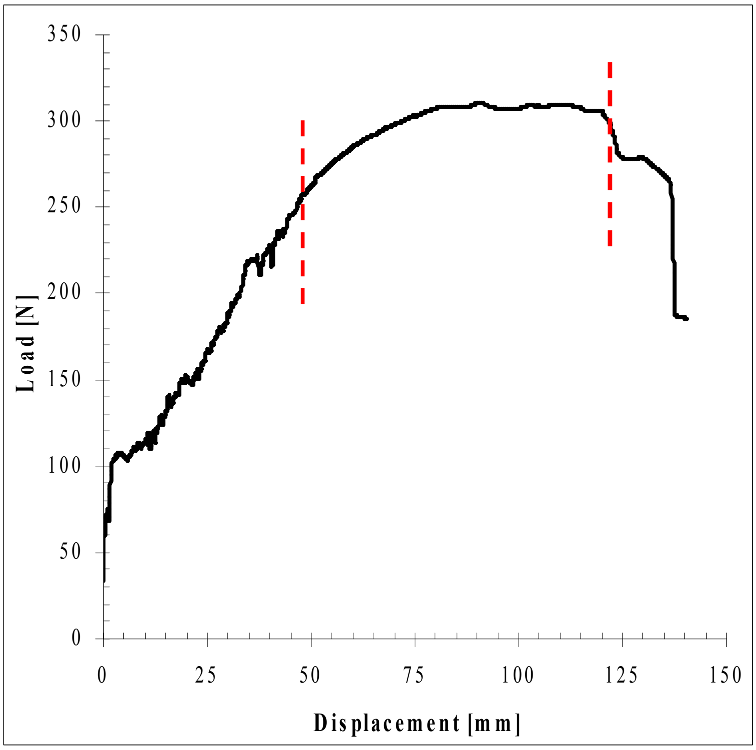


Figure 11. Peel experimental test curve obtained for the best trade-off Pareto solution with composition corresponding to CR=0.011198 [mm/min], PS=7.985 [N/mm] in Figure 10.

The validation results for peel strength are shown in Figure 11. Since the perfect anchorage of the adhesive to thermoplastic rubber (TR) in peel strength test the observed failure was cohesive. This failure occurs between the two vertical dashed lines as shown in Figure 11. Over a load equal to 258 N corresponding to first vertical dashed line, the experiment is driven to trial the

TR material instead the adhesive. This change of test conditions increases the load because the strength of TR is higher than the strength oh adhesive joint. The final failure occurred after the second vertical line in the TR material. From the previous considerations a mean failure load of adhesive joint is taken for peel strength calculation.

The peel strength per unit of width was determined by the ratio between the force and the width of the overlap joint that is equal to 30mm as referred in Section 3.2. So, the experimental peel strength value of 9.4 N/mm is considered, which is slightly upper the numerical result.

The same best trade-off solution with composition corresponding to CR=0.011198 [mm/min], PS=7.985 [N/mm] in Figure 10 is considered for creep rate experimental test. The complete creep rate experimental test curve is shown in Figure 12.

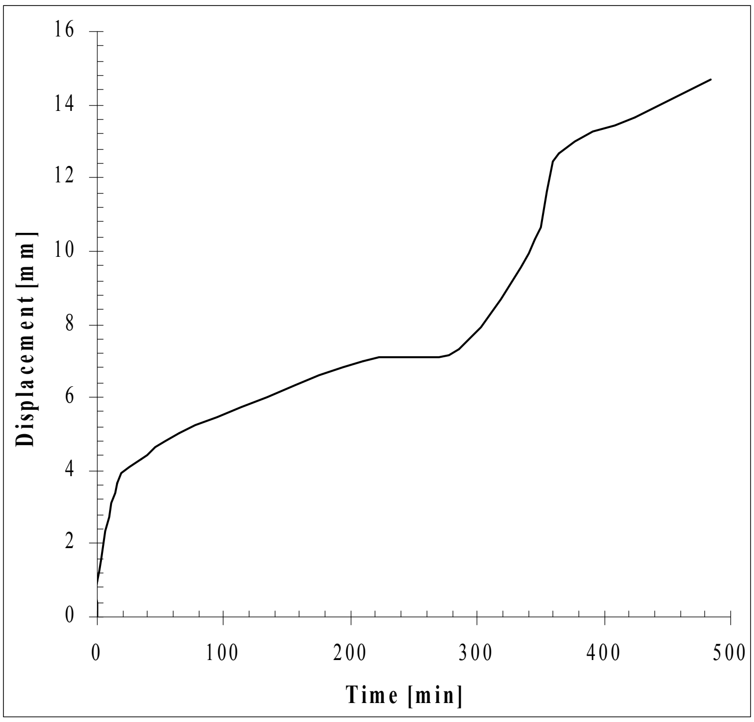


Figure 12. Creep rate experimental test curve (complete) obtained for the best trade-off Pareto solution with composition corresponding to CR=0.011198 [mm/min], PS=7.985 [N/mm] in Figure 10.

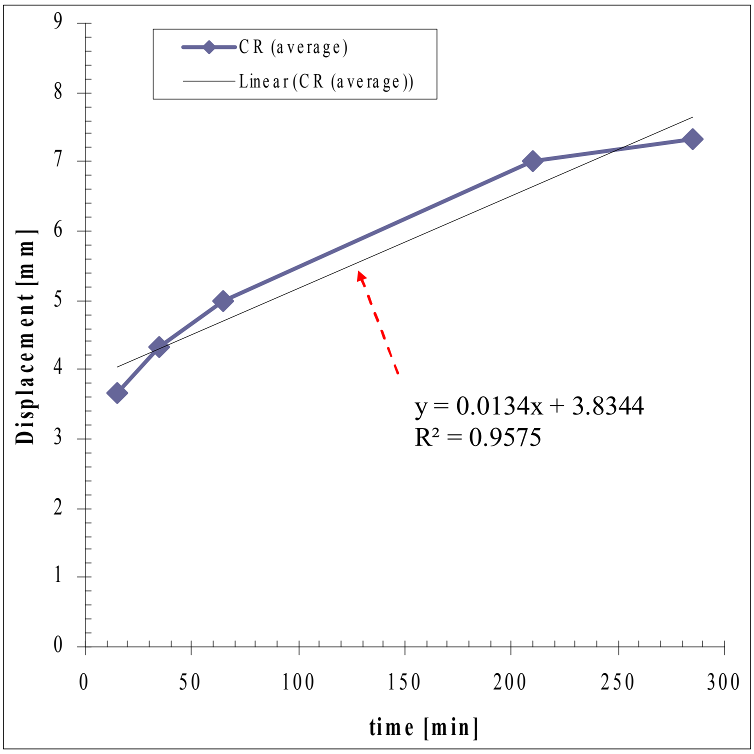


Figure 13. Creep rate experimental test curve (second phase) obtained for the best trade-off Pareto solution with composition corresponding to CR=0.011198 [mm/min], PS=7.985 [N/mm] in Figure 10. Linear regression of experimental values is plotted.

Since the primary and the tertiary phase are ignored on the calculation of the mean of the separation lengths of the bond only the secondary phase in curve plotted in Figure 12 is considered to evaluate the creep rate as referred in Section 3.2. The creep rate experimental test curve for the second phase is shown in Figure 13. The slope of the line obtained by linear regression of the experimental results corresponds to the creep rate. This experimental value is equal to 0.0134 mm/min, which is close to the numerical one, CR=0.011198 mm/min.

6.5 Results and discussion of global sensitivity analysis (GSA)

The GSA indices are obtained through ANN-Monte Carlo approach based on the algorithm described in Section 5 [19, 31]. Using the optimal configuration

$\mathbf{P}_{\mathrm{ANN}}{}^{\mathrm{opt}}$ a Monte Carlo simulation procedure is implemented aiming to study the sensitivity of the structural response of adhesive joint relatively to design variables that are the weight composition of raw materials. The referred algorithm is designed to obtain the first-order global sensitivity index of Sobol as defined in Equation (23). Two normalized Sobol indices are calculated as follows,

$$S_i(CR) = \frac{var\left(E\langle CR \mid x_i \rangle\right)}{var(CR)} \tag{24}$$

$$S_i(PS) = \frac{var\left(E\langle PS \mid x_i \rangle\right)}{var(PS)} \tag{25}$$

The above sensitivity indices are used to establish the relative importance of the design variables [19, 31]. According the theory presented in Section 5, the samples size values $N_f = 50$ and $N_r = 100$ are used to obtain the conditional probability for Sobol index. Two sampling procedures are simulated using the optimal $\mathbf{P}_{\mathrm{ANN}}{}^{\mathrm{opt}}$ and the following aspects are determined:

- the contribution of the variance of the conditional expectation, $var\left(E\langle CR|x_i\rangle\right)$ for total variance of creep rate, *var*(C*R*);
- the contribution of the variance of the conditional expectation, $var\left(E\langle PS|x_i\rangle\right)$ for total variance of peel strength, *var*(*PS*).

After, one first-order Sobol index per design variable x_i is obtained using the equation (24). The histograms in Figure 14 show the importance of the design variables measured by first-order Sobol index S_i. Figure 14 shows the contribution (%) of the variance of the conditional expectation, $var\left(E\langle \beta_j|x_i\rangle\right)$, for the total variance of β_j, *var*(β_j), where β_j can be creep rate or peel strength.

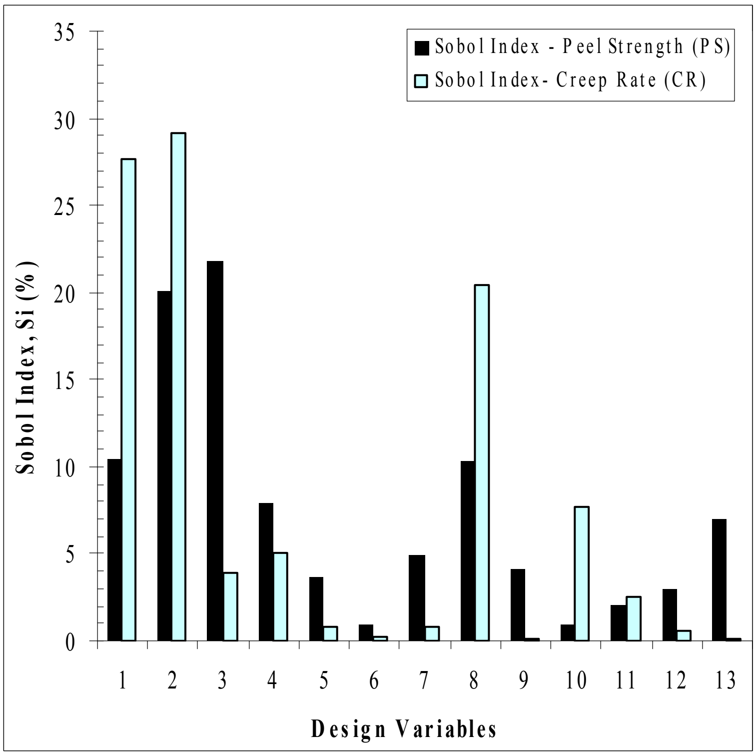


Figure 14. Importance measure of the input design variables by first-order Sobol index for Creep rate and Peel strength

The performance of the adhesive joint is very sensitive to the influence of some weight compositions of raw-materials. The sensitivities depend on the considered performance measures. When the performance is measured by creep rate, the design variables such as weight percentages on polyurethane (material 1 and 2), coumarone-indene resin (material 8) and the additive fumaric acid (material 10) are the most sensitive. If the performance is measured through the peel strength, the design variables such as weight percentages on polyurethane (material 1, 2 and 3), colophony and coumarone-indene resins (material 4 and 8) and chlorinated rubber as additive (material 13) are the most sensitive.

However, in relation to weight percentage of colophony (material 4), the sensitivity is in the negative direction for the creep rate objective minimization. This means that it is a resin when considered on the adhesive composition of the formulation there is an increase of the creep rate. So, this explains why the results obtained in second stage of the optimal design procedure did not consider the colophony in the optimal solution as shown in Figure 10.

Although the contribution of the additives is related with the improvement of mechanical behavior of PUs and resins, their influence on peel strength is shown through the sensitivities. However this is not observed for the weight percentage of Coumarone-Indene (material 8).

The GSA histograms in Figure 14 can help the designer to decide on the most important design variables to be considered for the optimization in second stage of the procedure. However, this must be implemented with care due to the synergetic effects between different groups of raw materials used in the composition of the adhesive joints.

7. CONCLUSIONS AND REMARKS

A mixed numerical-experimental approach capable to predict and optimize the performance of the footwear adhesive joints, based on the weight composition of used raw materials was presented. The proposed approach is supported by multi-objective design optimization concepts applied to the creep rate minimization and the peel strength maximization under technological constraints. The proposed approach is implemented considering two stages: (i) definition of the physical model based on planned experimental measurements and development of the ANN approximation model; (ii) the development of the MDO algorithm that is the engine search of the bi-objective optimization based on the weight composition of adhesive joints.

First of all, the set of experiments are planned using the Taguchi method aiming to obtain a good relationship between performance measures and design variables – weight composition of raw materials used in adhesive joint. After, considering the experimental results obtained for Taguchi design points as input/output patterns, an Artificial Neural Network (ANN) is developed based on supervised evolutionary learning using a genetic algorithm.

Secondly, a MDO algorithm based on dominance concepts and evolutionary search is proposed aiming to build the optimal Pareto front. The optimal design of adhesive composition to achieve the targets of minimum creep rate and minimum inverse peel strength (maximum peel strength) under manufacturing constraints is performed. The model uses the optimal ANN previously developed to evaluate the fitness functions and the constraints of the optimization problem.

Finally, a ANN-based Monte Carlo simulation procedure is implemented aiming to study the sensitivity of the creep rate and peel strength of the adhesive joint relatively to design variables - weight compositions of raw materials. In particular the Sobol indices for global sensitivity analysis are used to establish the relative importance of the design variables.

The results show the robustness of the proposed approach to build the optimal Pareto front enabling to establish the trade-off between minimum creep rate properties and minimum inverse peel strength (maximum peel strength) of the footwear adhesive joint using the weight composition of raw material constituents as design variables. The optimal results for both performance functions based on proposed approach are reached when large quantities for PUs and for some additives are considered. The performances of adhesive joints measured by creep rate and peel strength are very sensitive to the influence of some PUs and in some way are moderately sensitive to additives.

The proposed MDO approach supported by experimental tests shows improved explorative properties of raw materials and can be a powerfully tool for the designers of adhesive joints in footwear industry. In particular, since the optimal Pareto front is obtained it is possible to consider alternative designs for adhesive joints.

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Compliance with Ethical Standards

The authors declare that they have no conflict of interest.

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