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Durability study of glues for exterior panel bonding

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Abbreviations

A and S Adhesives and Sealants

ATR Attenuated Total Reflection

BSD Back-Scattered Electrons

CSPE Chlorosulphonated polyethylenes

DMTA Dynamic Mechanical Thermal Analysis

DSC Differential Scanning Calorimetry

DTG Derivative Thermogravimetry

EB Electron Beam

EVA Ethylene vinyl acetate terpolymer

IR Infrared (radiation)

MS Modified Silicone

PA Polyamide

PB Polybutylene

PC Polycarbonate

PUR Polyurethane

PVA Polyvinyl alcohol

PVAc Polyvinyl acetate

PVC Polyvinyl Chloride

QC Quality Control

RH Relative Humidity

SBS Poly(styrene-butadiene-styrene)

SE Secondary Electrons

SEM Scanning Electron Microscopy

SPE Silane-terminated Polyether

SPUR Silane-terminated poly(urethane-urea)

T_g Glass transition temperature

TGA Thermogravimetric Analysis

UV Ultra Violet

VOC Volatile Organic Compounds

Nomenclature

ALW PVC-EVA by Alwitra

BIT Bitumen Bounder with E-KV-4 waterproofing reinforcement

Black Versabond black

COV DAS-Panel Coveme Black

DUN DAS-Panel Dunsolar

EPDM *Ethylene Propylene Diene Monomer* rubber by Firestone

Grey Adheseal Grey

SIKA PVC by Sikaplan

TPO *Thermoplastic polyolefin* by Tremco

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Abstract

The present work deals with the durability study of two polymeric adhesives, used for structural applications such as manufacturing of vehicles, but mainly for panel bonding in the building field. The investigated products are provided directly from a company, PCS Innotec International NV, as part of a project with the Eindhoven University of Technology (TUe) and the Materials Innovation Institute (M2i).

Structural adhesives are widely employed because of their many advantages: they are cheap and easy to apply, allowing to save weight in the whole structure and preventing corrosion problems. However, in outdoor applications, the durability of polymeric joints is an issue: the effect of weathering, temperature variations, presence of UV and other factors can degrade the adhesive. The purpose of this dissertation is to study the durability of two adhesives, namely Versabond and Adheseal, focusing on the weather effects that may create problems for long lifespan applications, common in the construction sector. For this reason, extended–term accelerated aging processes are performed, simulating likely conditions such as exposure to high relative humidity or submersion in stagnant water. Moreover, the substrates considered are made of panels used for facades and roofs, such as EPDM, PVC or Bitumen.

Firstly, the degradation has been studied from a chemical, physical and microstructural point of view by means of FTIR, TGA, DSC and SEM, to investigate the water-related aging effects. To corroborate these results DMTA is used to determine the glass transition temperature as a parameter to compare reference and aged samples. Even if no important chemical degradation is found, the lap shear tests report a decrease in the mechanical properties of both, when subjected to the harsh conditions simulated. Finally, water absorption tests proves that water penetrate into the adhesive and degradation occurs mainly at the interface with the substrate. Given the strong dependence of the results on the material, that constitutes the substrate, this work opens the door to study the role of plasticizers, which could explain the different kind of degradation found.

Sommario

Il presente lavoro riguarda lo studio della durabilità di due adesivi polimerici, utilizzati per applicazioni strutturali come la produzione di veicoli e l'incollaggio di pannelli nel campo dell'edilizia. I prodotti sono forniti direttamente dalla PCS Innotec International NV, nell'ambito di un progetto con la University of Technology di Eindhoven e il Materials Innovation Institute.

Gli adesivi strutturali sono impiegati per i loro numerosi vantaggi: sono economici e facili da applicare, consentendo di risparmiare peso e prevenire problemi di corrosione. Tuttavia, nelle applicazioni all'esterno, l'effetto degli agenti atmosferici, le variazioni di temperatura, la presenza di raggi UV e altri fattori possono causare la degradazione dell'adesivo.

Lo scopo di questa tesi è di studiare la durabilità di due adesivi, chiamati Versabond e Adheseal, concentrandosi sugli effetti metereologici che possono creare problemi per applicazioni di lunga durata, tipiche del settore edilizio. Per questo motivo, si eseguono processi di invecchiamento accelerato a lungo termine, simulando condizioni probabili come l'esposizione a un'umidità relativa elevata o l'immersione in acque stagnanti. Inoltre, i substrati utilizzati sono presi da pannelli realmente impiegati in edilizia, come EPDM, PVC o bitume, usati in tetti e facciate.

Innanzitutto, la degradazione è stata studiata dal punto di vista chimico, fisico e microstrutturale mediante FTIR, TGA, DSC e SEM, al fine di esaminare da diversi punti di vista gli effetti legati all'acqua. A conferma di questi risultati, sono state condotti analisi dinamico-meccanico-termiche per determinare la temperatura di transizione vetrosa, parametro necessario per confrontare i campioni di riferimento con quelli invecchiati. Pur non riscontrando alcun importante degrado chimico, entrambe le colle mostrano una diminuzione delle loro proprietà meccaniche a causa delle severe condizioni simulate, come riportato nei risultati ottenuti con il lap shear test. Infine, i test di assorbimento d'acqua ne confermano la penetrazione nell'adesivo, provando che la degradazione si verifica principalmente all'interfaccia tra il substrato e l'adesivo.

Introduction

In the field of structural adhesives, the use of polymer-based adhesives has grown in popularity, thanks to the advantages exhibited, such as low cost, ease of processing, weight saving and corrosion resistance. In particular, during last years, the interest in hybrid systems is increasing. These adhesives are customized to exploit the best properties of two or more families of polymeric resins, with the aim to fill the gap in application thanks to new, promising formulations.

Having to deal with building and automotive sectors, where the role of a single adhesive bond is crucial, the producer company must be sure of its product features and limits, before guaranteeing it for the required lifetime. The drive to market new high-performance products faster and faster, requires carrying out tests reduced over time. The only way to fulfill this necessity is to employ accelerated aging tests, associated with the simulation of specific conditions, like moisture or chemicals presence, freeze and thaw, UV rays exposition, salt spray, but also combinations of them.

Manufacturing companies have designed their own tests to obtain results in a short period of time, sometimes by means of temperatures that can bring effects not observed in real life, but also reaching a simulated lifetime not comparable with the real one, like in case of panels for facades or roofs. To consolidate the study and ensure the durability of its products, PCS Innotec International NV has joined a project in collaboration with the University of Technology, Eindhoven (TUe), under the supervision of the Materials Innovation Insitute (M2i). The present work is part of this two-years project carried out within the building materials group in the Department of the Built Environment at TUe.

The purpose of this dissertation is to deepen the knowledge of two specific products, *Versabond* and *Adheseal*, focusing on the degradation mechanisms and effects that may take place during and after a long term accelerated aging test.

The studied polymeric adhesives are part of the previously mentioned hybrid systems. In particular, *Adheseal* is a silane-modified polyether, while *Versabond* is a silane-terminated polyurethane. They show optimal performances in joining dissimilar surfaces, where they are already implemented. Therefore, the possibility to extend their field of application is interesting, for the company, but also to create new building systems, useful to the community. For this reason, longer and different kinds of aging are needed, together with more specific tests.

It is known that there are several issues concerning the durability of a polymeric joint: weathering effect, temperature variations, presence of UV rays and other factors can cause aging or degradation. In the first chapter many of these degradation agents are introduced, together with an overview about the how durability is assessed and the laws that regulate artificial aging. A general context about structural adhesives and their properties clarifies the reasons why these products have been largely applied since the 40s'. The physical principles of adhesion, the main formulations and morphologies of adhesives are briefly reviewed, for then moving the focus closer to the materials involved in this study, describing them from a literature point of view. The work goes on introducing the methods employed to characterize the glues and assess their degradation.

In the second part of the elaborate, the results obtained are exposed. The first phenomenon studied is the UV degradation, which is a threaten for polymers in outside applications. This radiation cannot affect the glues since all the substrates considered are not UV-transparent. Then several thermo-chemical techniques are involved, always differentiating the results according to the material investigated and the aging method it has been subjected to. The accelerated aging in fact takes place in presence of a constant relative humidity or with immersion in water of the specimens considered. While FTIR spectra show that only moderate effects can be detected in these glues, the other characterization systems used, thermal-based but also SEM, display phenomena that can be totally understood only if associated with the results in the last two chapters.

Especially the lap shear mechanical test shows the effective degradation in the mechanical and adhesive properties of the studied glues. Finally, a gravimetric analysis is presented, together with other tests related to water absorption, either within the adhesive or at the interface with the substrate. These measurements allow to quantify and understand water penetration mechanism and its correlation with the changes in mechanical properties.

Chapter 1

Structural adhesive bonding

1.1 State of the art

The main goal of an adhesive is to bind surfaces together and, to do that, certain mechanisms have to take place at the microscopic level (and even closer). These necessary interactions are those formed by dissimilar particles or surfaces in contact: their tendency to join is named *adhesion*. For this reason, before introducing adhesives and their properties, it is fundamental to briefly expose on which physical principles their functioning is based.

1.1.1 Adhesion

One of the most important features in adhesive bonding is the condition of the surfaces to be joined, which needs to be prepared or pretreated to guarantee bonding quality. Two important properties depend on the substrate condition: adhesion and cohesion. During curing, the adhesive passes from a liquid or pasty state, in which the adhesive wets the substrate activating molecular interactions, to a solid state, when cohesion (adhesive internal strength) is built up. In this way adhesion affects the bonding strength [4]. Ideal adhesion is in fact related to the thermodynamic work of adhesion, the reversible work required to perfectly disjoin an unit area of interface between an adherend and an adhesive in a medium.

Mechanisms of adhesion

There are different models of adhesion, with as many field of application. These different mechanisms can be present also together (e.g. since all adhesive bonds put molecules in close contact, physical adsorption is always a contribution).

Physical bonding comprises the interactions of dipole forces, Hydrogen bridges (between very polar groups) and dispersion forces (Van der Waals forces).
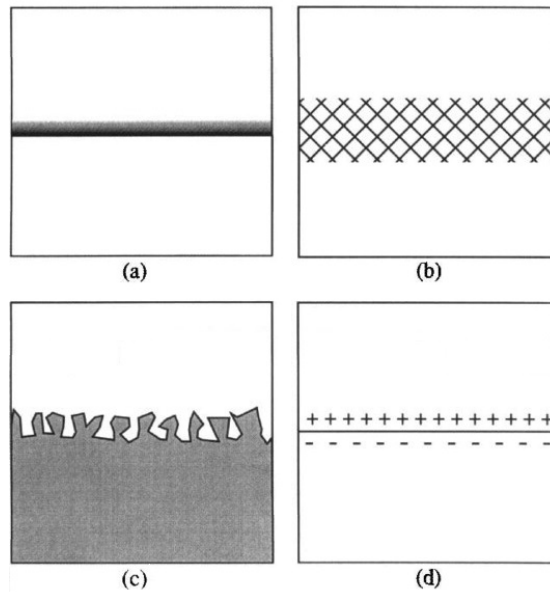
Figure 1.1: Four mechanisms of adhesion: (a) adsorption (contact adhesion), (b) diffusion, (c) mechanical interlocking, (d) electrostatic [1].
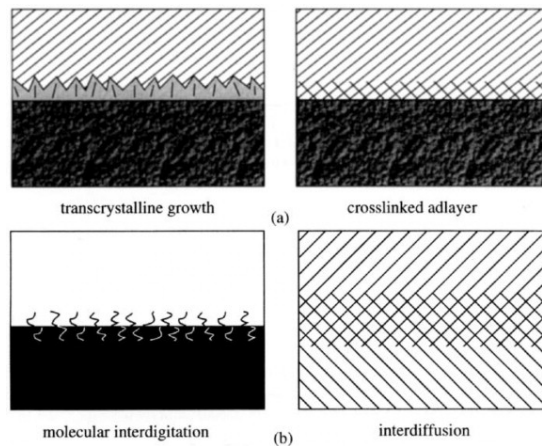
Figure 1.2: Different types of interphases: (a) contact and (b) diffusion ones [1].

Chemical bonding occurs when there is a reaction between groups of the adhesive and of the substrate surface, bringing to the formation of either covalent, ionic or complex bondings.

Adsorption leads to contact adhesion through molecular interactions across a well defined interface: the polymer self-organizes to give transcrystalline growth, in Fig. 1.2, when in contact with a hard or highly polar surface. For instance, in thermosetting adhesives (like polyurethanes) the degree of crosslinking is often very different near the interface and, according to the

adherend composition, an interphase is formed.

Diffusion takes place in the bonding of polymeric adherends and adhesives, especially in case of autoadhesion. Given a sufficient time frame and an adequate thermodynamic compatibility between the two involved materials, the mobile polymer chains (not crosslinked yet) will inter-diffuse, forming an interphase through diffusion or interdigitation, as in Fig. 1.2.

Mechanical interlocking is exploited by roughening the adherend surface, as shown in Fig. 1.1.

Electrostatic interactions across interfaces play a role in adhesion: the surfaces in contact form an '*electrical double layer*'. Its contribution to bonding strength is rather small [1].

1.1.2 Polymers and adhesives with structural application

With more awareness on the laws ruling adhesion as an interatomic and intermolecular interaction, the focus can be moved on adhesives themselves. They are materials that are applied to form a thin interlayer between solid substrates or adherends, with sufficient adhesive and cohesive strength to form a strong and durable bond [13]. This definition includes a lot of materials, from cement to glues. In the last 80 years, the science and the technology of adhesives and adhesion has developed significantly and nowadays the adhesives used in most technical applications are based on synthetic polymers [14].

Polymers are substances composed of macromolecules, which are characterized by the multiple repetition of one or more species, made of atoms or groups of atoms. These constitutional repeating units are linked to each other by covalent bonds. A monomer is the substance from which the polymer is obtained in a process called polymerization [15].
A polymer can be a hard and stiff solid or a soft and flexible elastomeric rubber, depending only on the use temperature with respect to a reference temperature called *glass-transition temperature*, T_g [2].

The different macromolecular architectures that are found in polymers have important consequences from the technological point of view.
Thermoplastics are linear or branched (with more than two terminations) polymers, so in both cases the molecular weight is measurable and, when heated above their glass transition temperature, they pass to a viscous liquid state. Therefore the material can be transformed more times just by bringing it in this state and, in case of linear polymers, thermoplastics are soluble in suitable solvents.
On the contrary *thermosets* are crosslinked polymers and so by heating they do not melt or soften, but rather become more rigid, because their macromolecules are chemically bound and cannot flow, even under thermal stress. For this reason

the forming operations are carried out simultaneously with the chemical crosslinking reaction: the transformation process is irreversible in this case. Finally, they are insoluble or at most swellable in solvents.

Different technologies derived from polymer science: plastics[1], rubbers or elastomers, fibers, surface finishes, protective coatings and adhesives. In particular structural adhesives are polymeric materials that are characterized by dimensional stability during the lifetime of the structure they join.
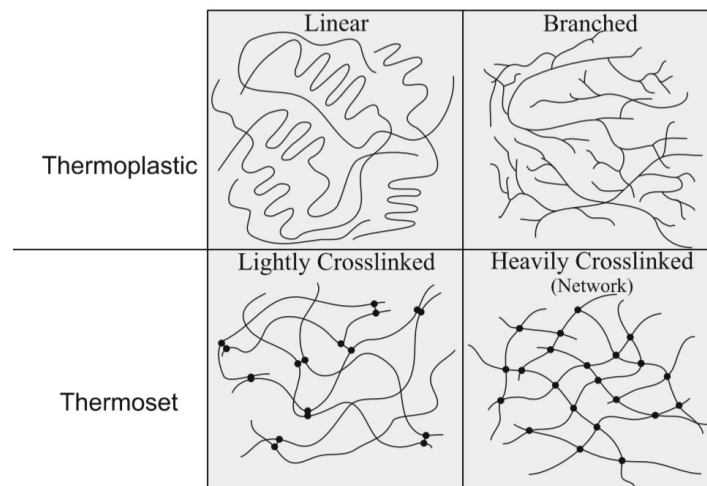
Figure 1.3: Variations in thermoplastic (top) and thermosetting polymers (bottom) [2]
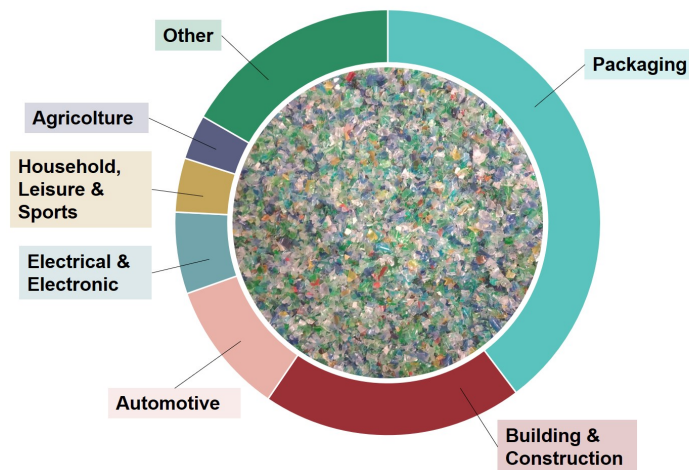
Figure 1.4: Distribution of European plastic demand by segment in 2018 [3].

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[1]the term '*plastics*' is commonly used to speak about all the technologies listed above

In Europe the market sectors with highest plastic demand in 2018, reported also in Fig. 1.4, are respectively packaging with 39.9%, building & construction 19.8% and automotive 9.9% [3]. These last two fields of application, together with aerospace and other industries, generally named as *structural*, have seen polymers growing in popularity in recent years, because of their advantages: low cost, ease of processing and maintenance, weight savings and corrosion resistance [2]. To give an example for the construction field, polymers are about 1% of the total volume of building materials, even representing the fourth major class after steel, wood and cement. The reasons can be found in the precautions adopted by this industry, which needs a lot of tests before abandoning well known and proven methods for new and promising ones. Moreover several regulations slow down further this process, to guarantee safety and durability of the structures [12].

1.1.3 Historical background of structural adhesives

In this context of *structural* polymers, not only rigid lightweight composites, but also adhesives must be considered, being employed in all the phases of the building industry, but also in the automotive production.
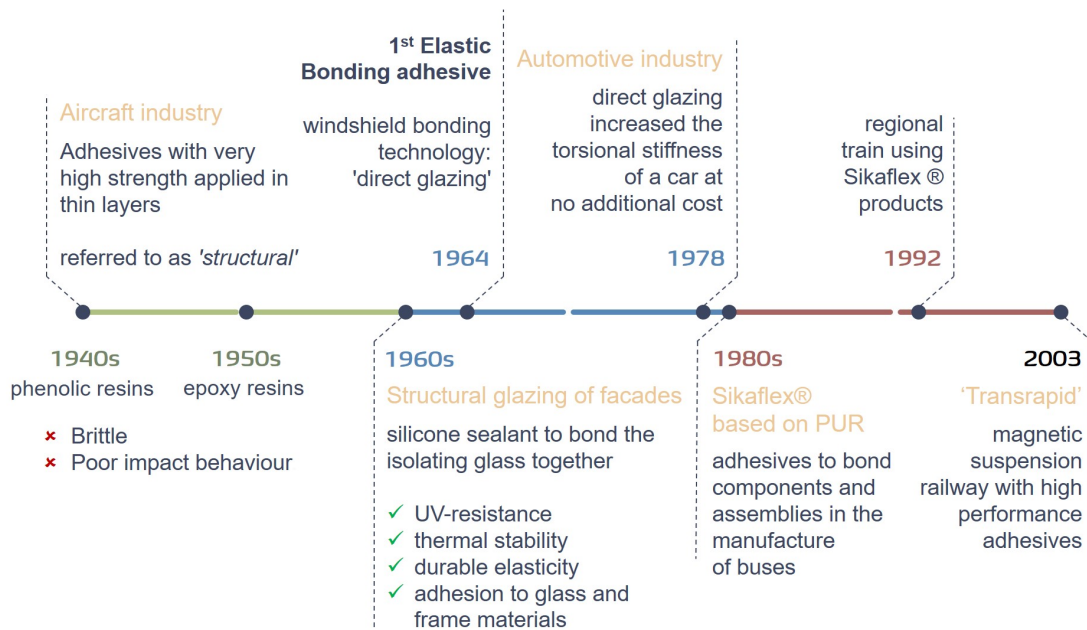
Figure 1.5: Elastic bonding and sealing in industry: historical background [4].

As explained in Fig. 1.5, the use of adhesives in industry started around the WWII for aircraft construction. Actually the 1st elastic bonding is reported in 1964, when *direct glazing* was performed by using a sealant cured to an elastomeric adhesive, which guaranteed good adhesion in facades. This new fastening technique was then extended to the realization of means of transportation, from cars

(Fig. 1.6) to buses, trucks or trains: in this way, the automotive industry reduced the vehicles weight, enhancing their efficiency and reducing the emissions [16]. The next step was to apply this technology to several manufacturing sectors [4], for producing containers, ships and boats, refrigerators, washing machines and in the realization of facades, roofs (Fig. 1.7), floors, windows, etc. An advantage of these elastic adhesives is an improved long-term durability, with respect to resins, their predecessors. This is related to their composition: elastomeric particles are added to improve the fracture toughness, while alumina or metal particles increase the tensile and shear strength.
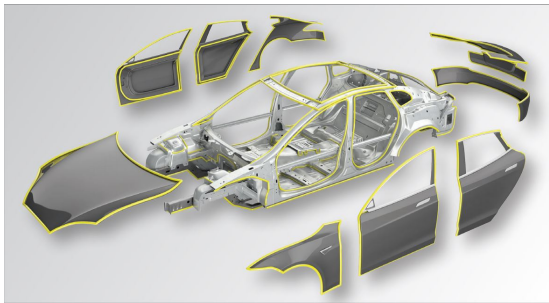
Figure 1.6: Adhesives application scheme in a car design

Figure 1.7: Application of a roofing adhesive

By using adhesives instead of the traditional bonding techniques, some important advantages are obtained:

- Thin sheets can be joined, also if made of dissimilar materials: wood, plastics, composites and metals, ensuring corrosion protection;

- A greater styling freedom is granted for the designer. Besides it, the manufacturing tolerance is compensated by using elastic adhesives, for which the thickness of the layer does not influence the joint strength;

- The even stress distribution of the joint brings to an higher fatigue resistance of the system. Moreover, no thermal distortion is imparted by using adhesives;

- Costs are reduced even though, as adhesives, polymers are more expensive than in the other forms of application. The economic benefits are due to several reasons: simultaneous sealing, lighter weight of the structure, less energy required, corrosion prevention.

Sealants

If on one hand adhesives were largely applied during the finishing trades of the building sector, on the other one the use of sealants increased in wall construction.

Nowadays the term *sealant* is used for all weatherproofing joint materials, or, more generally, those substances that separate a joint from any medium to which it is exposed. Therefore sealants are usually made of synthetic elastomeric polymers, in order to be pourable or extrudable before curing. After it, they are able to become elastomeric materials, insulating not only from moisture, but from air and heat too. Sealants are present in the market in three main forms:

○ Putty-like mastics

○ Non-cured tapes

○ Cured gaskets

Mastics are employed either in one or two-component formulations: in the first case no mixing is needed and they show a longer pot life. The curing process is moisture-dependant: after the application, a surface skin is formed in a few hours, while complete curing can take several days. It must be underlined that nowadays also elastic adhesives act as sealants, protecting a joint from gasses, water or chemical attack.

1.1.4 Adhesives chemistry

Table 1.1: Material based classification of adhesives and sealants [12].

Adhesives		Sealants
Thermoplastic	**Thermosets**	Silicones
PVAc	Phenolics	PUR
PVA	Epoxies	Polysulphides
PVC	Polyaromatics	Polymercaptans
Acrylics		CSPE
PA		Polyacrylics
PC		Butyl rubbers
PUR		Polychloroprene
Cellulose		PB
		Oil based caulks

As in Table 1.1, adhesives and sealants can be classified considering their chemical composition or, more correctly, according to the base resin they are made of, either a polymer or a rubber [12]. The general properties of the final product are in fact determined from this main constituent, even though other components in quantities from $> 10\%$ to $< 0.01\%$ are usually added to modify specific properties.

In particular, commercial structural adhesives are often characterized by high modulus and strength, thanks to the use of:

- Epoxy (or epoxide)

- PU - polyurethane

- *Reactive / toughened / anaerobic* acrylic

- Cyanoacrylate

- Silicone

1.1.5 Adhesives morphology

The second way to classify adhesives is to distinguish them according to their physical forms, as previously done for sealants:

○ Two-part liquids/pastes

○ Single-part liquids/pastes

○ Sided tapes

○ Films with or without carrier

○ Single-part solids (blocks, chips, rods)

Adhesive structure is for sure chemistry-related, but also driven by the final application: the morphology and the **curing mechanism** are interdependent. For two-part adhesives, in some cases contact can be enough to start the reaction between them (mainly for free radical-based), while sometimes a certain level of mixing is needed to complete the curing.

On the other hand, single-part systems can be constituted either by a mixture of two components (e.g. solid and liquid) in a non-reactive state or by a single substance which needs an external source to initiate the curing, such as moisture or UV radiation.

Finally pressure sensitive tapes usually show a non-chemical curing, while adhesive films are solid single-part systems, supported by a carrier substrate [5].

1.1.6 Adhesives mechanical properties

The third and last way to categorize adhesive systems is related to their strength and stiffness: they can be divided into rigid, flexible structural and elastic bonding groups, while sealants represent a separate class. As shown by the scheme in Fig. 1.8, these categories have different values of reversible elastic deformation, which is a typical feature of elastomers: these materials do not undergo plastic flow thanks

to their open network structure due to vulcanization, a mild chemical crosslinking. The other property reported in the graph is the shear modulus, which defines the degree of stiffness or load transfer.
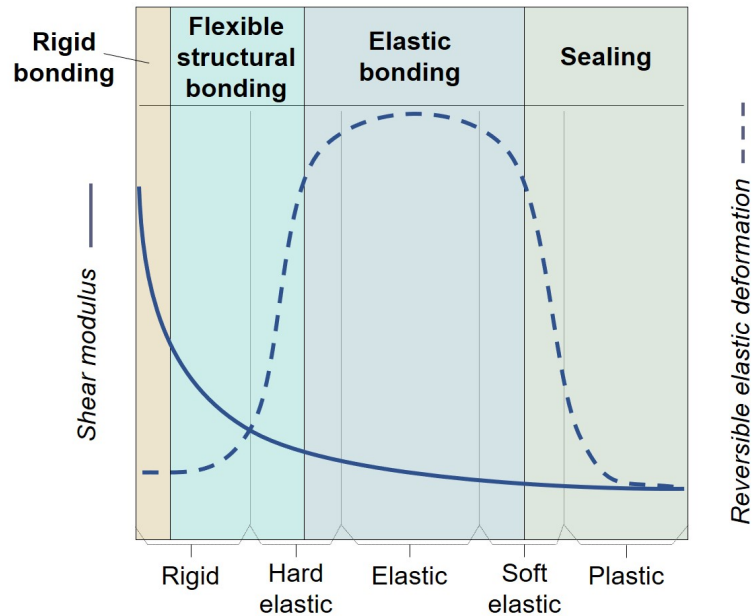
Figure 1.8: Different adhesive and sealant systems: reversible elastic deformation [%] and shear modulus [MPa] are reported [4].

Rigid bonding is widely employed in structural applications. It is characterized by a peak load at the edges, which limits the strength of the bonded joint and, combined with a low ($\sim 2\%$) elongation, results in poor impact resistance.

Elastic bonding generally exhibits a lower stress level. The ability to undergo and recover deformation makes these adhesives resistant to sudden stresses or short overloads, like in impacts between moving vehicles. This capability depends also on the strength, but mainly on the fracture energy. It is the energy required to deform the adhesive before failure occurs and it is proportional to the area beneath the tensile lap-shear strain curve (Load vs. Displacement of bonded structures).

Flexible structural bonding is the combination of the two first regimes described and allows to optimize mechanical properties like strength and stiffness, but also to maximize the elongation, see Fig. 1.9. The load transfer has values in between that of rigid and elastic adhesives. Given these considerations, it can be said that flexible structural adhesives perform better than the rigid ones, thanks to their enhanced elasticity, regarding especially impact, crash and durability [4].
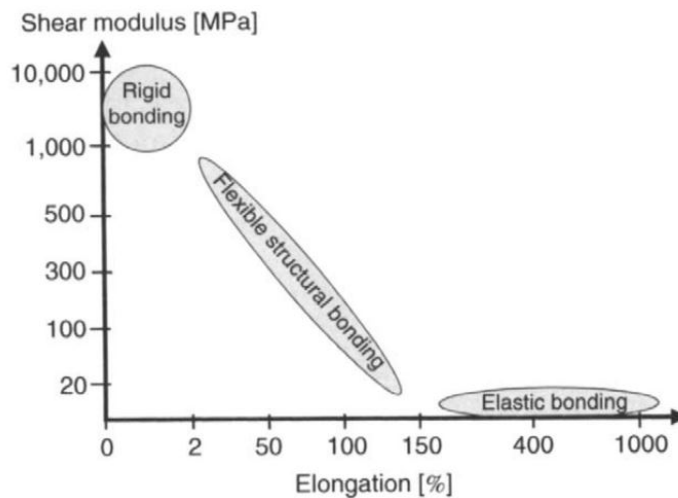
Figure 1.9: Shear modulus and elongation at break [4].

1.2   Conventional modern glues

In this section firstly polyurethanes and Silicones are presented, as an introduction to the following description of hybrid adhesive systems, which constitute the products analyzed in this work too.

It is necessary to say that, even knowing the main composition of an adhesive, is hard to be really aware of what it actually contains and therefore to forecast its properties and their behaviour in time. Adhesives are indeed complex mixtures of materials, comprising reactive agents, rheology modifiers, fillers to control shrinkage, thermal expansion control agents, adhesion promoters, toughening agents, colourings, cure initiators, and so on.

Polyurethane

These adhesives, often abbreviated to PU or PUR, are able to bond many materials, including plastics, glass, stone and metals. In Fig. 1.10, PURs encompass a wide area, proving to be the most versatile adhesives. Their mechanical properties can indeed be adjusted, from soft and elastic, rubber-like, to very rigid, by varying crosslinking density, chain length, molecular building blocks and number of functional groups. Polyurethanes are mainly built up via difunctional and trifunctional OH-terminated molecules (Fig. 1.11), which react with di- or tri-isocyanates. The chain length and stiffness are related to the mechanical properties of the final polymer: in case of polyether chain, flexibility and hydrophilicity are granted, while polyesters give more rigidity. Stiffness is strongly influenced by the concentration of trifunctional molecules too: they determine the crosslinking density, therefore they are often used to produce structural adhesives, to guarantee a covalent three-dimensional network.
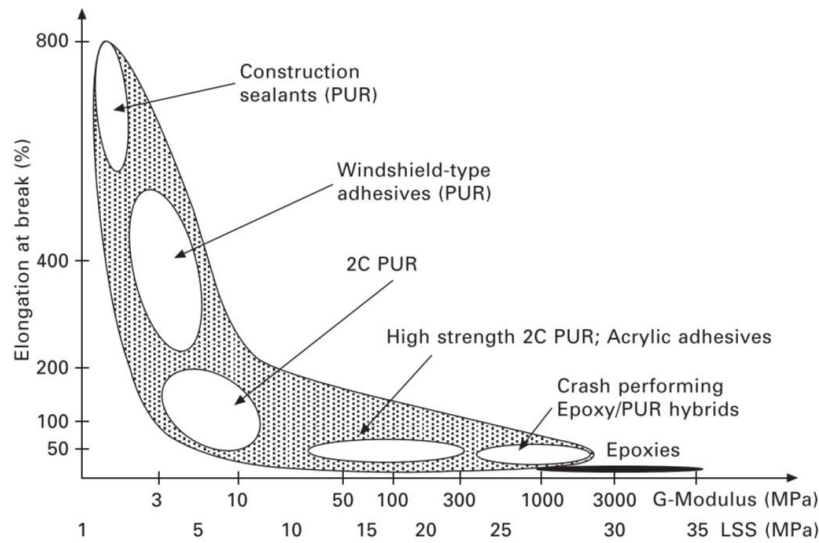
Figure 1.10: Most commonly used structural adhesives in terms of their shear modulus (G), elongation and lap shear strength (LSS) [5].
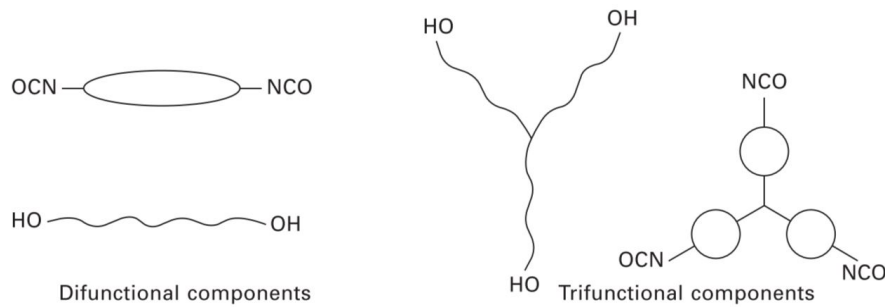
Figure 1.11: Schematic building blocks for polyurethanes [5].

The joints bonded through polyurethanes show a good resistance to impact and a better cryogenic temperature strength than most other adhesives. Their formulation can be either one-part (1C) or two-part (2C) based. Single-part formulations are partially polymerised and chemically stable until cure is initiated through exposure to atmospheric moisture. The curing rate is controlled by diffusion: it is relatively slow, the full cure can last from hours to days, and environmental conditions like temperature and humidity significantly influence the curing speed. Among all the possible applications in the construction, automotive and marine industries, polyurethanes are used for the frame structure of buses, but also to install windshields, headlights and other parts in automobiles. They are employed in the production of sandwich insulation panels, used in buildings and finally on trucks, wooden structure and windows.

Silicone

Silicone adhesives are appreciated for their flexibility and their ability to stand a wide temperature range (from cryogenic conditions to over 250°C). They are available in one-component form, in which curing starts with the diffusion of atmospheric moisture. The cure mechanism is condensation[2], with the resulting formation of silanol (Si-OH) groups and either alcohol or (acetic) acid. Among the main applications for silicone adhesives, there is glass bonding, either as structural glazing on buildings or for tank fabrication. They are applied not only in automotive, aerospace, solar photovoltaic industries, but thanks to their high temperature resistance and flexibility, also the production of many electronic and medical devices requires them [5].

1.2.1 Silane-Terminated polymers

In Europe silane-modified polymers have been used to formulate adhesives and sealants since the late '80s [18]. They are hybrid systems in which the formulation is "*customized*" in order to exploit the best properties of two or more families of polymeric materials. Also the two glues analyzed in this work can be counted among hybrid adhesives, in both cases with a silane termination, but with a different backbone.

Polyurethane-Hybrids (SPUR) are a kind of silane-terminated adhesive and, together with modified silicones (MS), they are able to provide no bubbling in curing, since gaseous release is prevented. Moreover, their adhesion on several substrates is guaranteed with almost no surface pretreatment.
Silane-terminated polymers crosslink by reacting with water and, as a consequence, alcohol is released.
Silane terminated polyether (also called SPE) contain two active dimethoxy-silane groups, resulting from the hydrosilylation of the vinyl group from the intermediate polymer. As well as polyurethane or silicone adhesives, MS are moisture curing single component systems, very flexible, providing a uniform stress distribution in assembly. Since peel and shear stresses are distributed over a large area, they show enhanced joint efficiency. However, their high flexibility and elongation show lower cohesive strength with respect to more rigid adherents, so a larger overlap and quantity of product are needed [5].
The presence of bubbles in standard PU materials is due to the reaction between their NCO groups and the water present in the air, giving CO_2. SPURs avoid this, because silanes bind to NCO and then the curing occurs by hydrolyzation and condensation, without releasing CO_2 [19]. As shown in Fig. 1.12 PUR-

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[2]In condensation polymerization molecules react because they contain mutually reactive chemical groups: there are at least two groups per molecule. In case of trifunciality, branching or crosslinking will result [17].

Hybrids can include either two or three functional silane groups, which bring additional advantages in SPURs' mechanical behaviour. It must be mentioned that the polyurethane core of SPUR adhesives makes them rather insensitive to moisture.
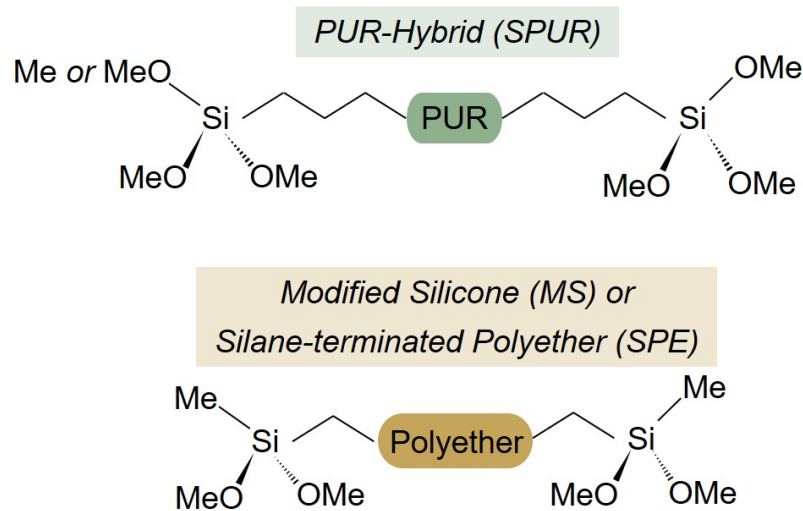
Figure 1.12: Functionality of PUR-Hybrid (silane group can be 2 or 3 functional) and MS systems (silane group is 2 functional) [4].

1.3 Durability issues in adhesives

Sealants and adhesives must withstand not only the mechanical forces acting on them but also the surrounding environment conditions. If affected by factors like temperature, moisture, chemical fluids and outdoor weathering, the mechanical properties of polymers may vary with time, due to changes in the molecular structure. Aging can be physical, when Variations take place in the molecular packing and their effects are fortunately thermoreversible. In case of modifications of the inter/intra-molecular bonding, chemical aging is involved, with irreversible consequences [2]. Aging is a threat for adhesives, both in the automotive sector, where joints must stand high stresses in a wide range of temperatures and in contact with liquid substances, and in outside applications, since weathering is a threat for many physical properties of the adhesives [12].

However long-term performance of bonded joints cannot be predicted just by knowing the properties of the adhesive and adherend's surfaces, since the complex set of phenomena that takes place at the interface require the testing of bonded structures.

1.3.1 Water

Water can be pointed out as a threatening agent against adhesives durability: it can penetrate in different ways inside the adhesive or into the interface with the substrate, with detrimental effects for adhesion, see Fig. 1.13.

Absorption of water in the adherent occurs with two possible mechanisms: inside the adhesive structure itself, as *free water*, often clustered in microvoids and causing plasticization[3], or as *bound water*, since hydrogen bonds are formed with the polymer, which undergoes swelling: in this case plasticization can be detected thanks to a decrease in strength and glass temperature (T_g). The ageing of the joints can be initially reversible and, by drying, the mechanical properties are recovered: this behaviour is more likely if temperatures are low. As the ageing process goes on, a degradation of the adhesive properties can occur, even more if enhanced by high temperatures.
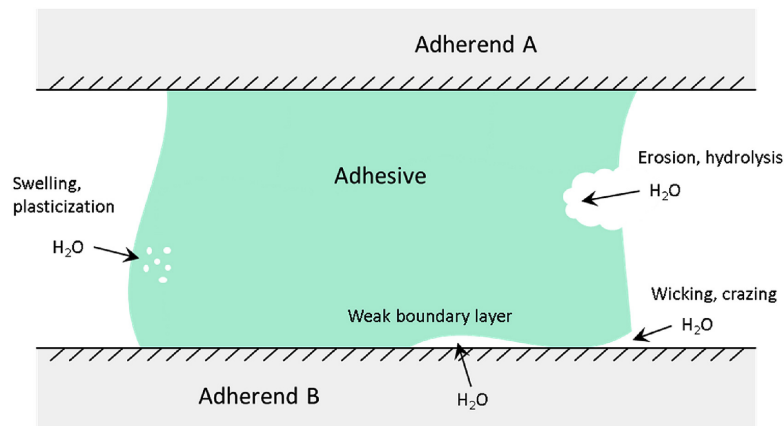
Figure 1.13: Four pathways by which water undermines the performance of adhesive bonds [6].

Some polymeric materials, particularly ester-based polyurethanes, suffer from 'reversion' in contact with water, losing hardness, strength, and in the worst cases, they can even liquefy if exposed to warm and humid air. This process is faster in flexible materials because water permeates them more readily.

There is also the possibility that water segregates at the interface between the adherend and the adhesive, weakening the bond (Fig. 1.14). Although it is hard to quantify the real amount of water present at the interface, in [21] it has been showed, by using neutron reflectivity, that the water concentration at polyimide/silicon oxide interface exceeded that of the bulk by more than 500%. This accumulation of water depends on the substrate considered: it occurs easily

---

[3]Plasticization is the absorption of small chemically benign molecules that migrate between the macromolecular chains, thus allowing the plastic part to lose stiffness [20].

in hydrophilic surfaces, which show high surface energy. Also the presence of contaminants at the interface can contribute to this phenomenon, such as hydrophilic unreacted resins, curing agents, additives and impurities. These substances can leach out from the adhesive during exposure to water [22].

Finally water, but also humidity, may penetrate into porous substrates, swelling it and causing movements that can become an issue for the functioning of the joint [11].
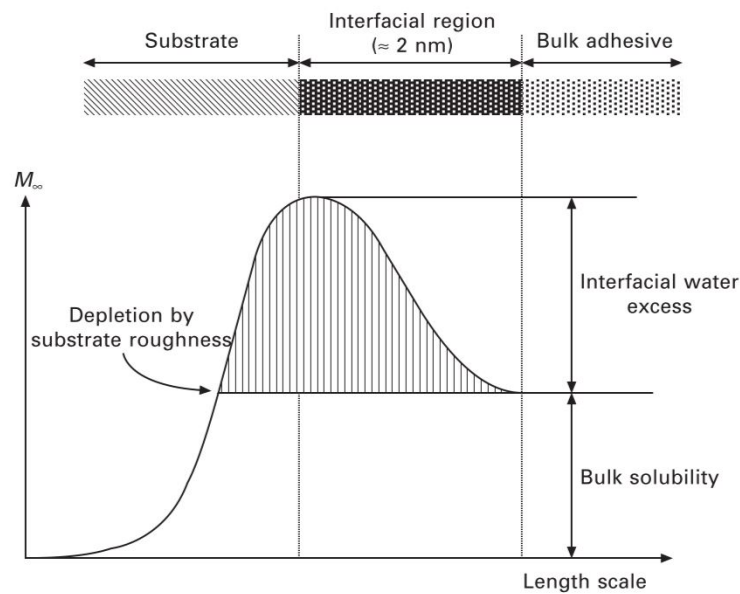
Figure 1.14: Schematic of water concentration profile near a polymer/substrate interface. The higher concentration of water at the interface is due to the stronger affinity of water for the substrate than the bulk polymer [5].

Moisture

Structural adhesives may lose strength when exposed to moisture, particularly at high temperatures. It diffuses into the polymer matrix, acting like a plasticiser, but with a long-term influence on the adhesion. Among the degradation mechanisms caused by moisture at the interface, there are hydrolysis of interfacial bonds, hydration of substrate oxide layer and cathodic delamination [5].

What is experience is that, in presence of moisture, the failure is initially cohesive, becoming then of adhesive nature, after some days. In particular, adhesive joints show a sudden drop in strength when exposed to humidity levels above a certain critical value. In [7] a mechanism of adhesion failure at the critical RH is proposed, based on the synergistic effects at the interface and in the bulk swelling. By increasing the humidity, the water present at the interface grows, decreasing the contact area between adhesive and substrate. On the other hand, swelling in bulk is due to its increase in solubility at the critical RH. The interfacial water

is compressed because of the stresses induced by the swelling, which are anyhow lower with respect to those in-plane, related to the adhesion itself. As a result, an out-of-plane expansion results in deformation of the interfacial water phase, contributing to decrease the energy requirement for adhesive failure with a new a normal force, Fig. 1.15.
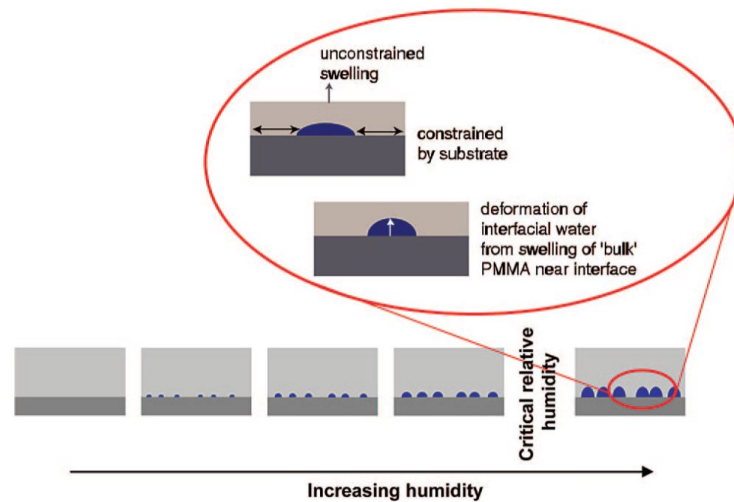
Figure 1.15: Schematic representation of how water concentration near the interface takes place at the critical relative humidity for loss of adhesion strength [7].

1.3.2 Chemicals

Chemical substances like salts, detergents, fuels and gases, which can be present also in aqueous solutions, worsening their effect, can be detrimental for the joint, especially in case of constant exposition. Moreover organic adhesives susceptibility to chemicals and solvents is enhanced at elevated temperatures: since more fluid is generally adsorbed by the adhesive, the degradation rate increases.

The permeation of chemicals through polymers is a mass transport and it is possible only as a combination of interrelated processes: dissolution in the polymer and diffusion through it.

Dissolution is the *absorption* of chemicals in the polymer. It depends on the affinity between the polymer and the absorbing molecules, on the volume available and on the concentration of chemicals. The solubility limit determines the maximum amount of chemicals that can be absorbed and depends in turn on the surrounding conditions.

Diffusion occurs when the already absorbed species pass through voids and gaps between the polymer molecules (Fig. 1.16), or by capillary attraction along the interface. The level of porosity is the key point, indeed the rate of this process depends on the diffusing species' and gaps' sizes. In case of different diffusing

species but with similar solubility parameters, the smaller ones will diffuse faster than larger molecules. Amorphous polymers are more susceptible because their *free volume*[4] allows solvent molecules to diffuse readily, especially in the rubbery state. Moreover these molecules enable segmental motion in the polymer, shifting T_g to lower temperatures [5].
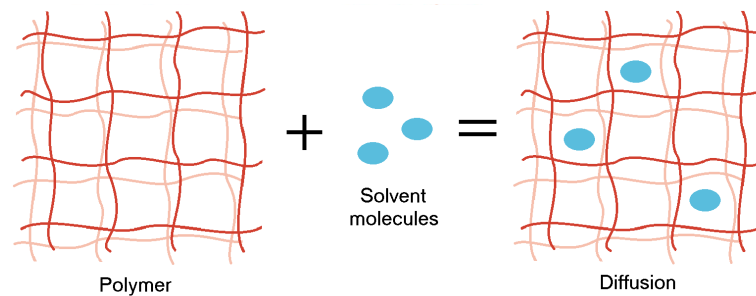
Figure 1.16: Schematic of solvent molecules diffusion through polymeric chains, redrawn from [8].

Among all adhesives, none of them can be used in all chemical environments, but it is quite easy to find an adhesive resistant to a particular condition. Generally, adhesives which are more resistant to high temperature have a better resistance to chemicals and solvents too.

1.3.3 Temperature

As already mentioned, temperature can amplify water and chemicals effect since it accelerates any absorption process. Besides this, thermal ageing takes place when an adhesive is kept above its T_g and the consequent molecular reorganisation can be observed as a change in the mechanical characteristics of the bond [23]. That is the reason why the possible overheating of the adhesive (e.g. in case of fire) must be considered at the design stage and failure prevented with additional safeguards. Adhesives' high temperatures behaviour depends on their macromolecular organization: in thermoplastic adhesives close to the glass-transition temperature, polymeric chains undergo plastic flow, deforming the joint and loosing cohesive strength.

Being thermosetting adhesives highly cross-linked networks of macromolecules, they do not have a melting point. Therefore many of them are suitable for high-temperature applications, even though their strength can be reduced because of thermal oxidation and pyrolysis. Usually, rigid polymeric structures adhesives are the best in tolerating high temperatures, especially if they have high softening temperatures, optimal oxidation resistance and stable chemical groups. Their

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[4]The free volume is the space between polymer molecules accessible to their roto-translational motions.

drawback is the difficulty of processing.

Especially in aerospace applications, bonded joints must stand cryogenic temperatures and, because of stress concentrations and gradients developed inside them, many problems arise. The principal causes are:

- Difference in thermal coefficients of expansion between adhesive and adherend;

- Shrinkage of adhesive in curing;

- Trapped gases during bonding;

- Difference in elastic modulus and shear strengths between adhesive and adherend;

- Residual stresses in adherends because of the release of bonding pressure;

- Inelasticity or plasticity in the adhesive or in the adherend.

What happens is that at cryogenic temperatures the elastic modulus may increase, making the adhesive not more able to bear the concentrated stresses, as it was at room temperature.

1.3.4 UV-radiation

Ultraviolet radiation is a component of sunlight and it is among the primary causes of damage for organic materials. The risk is to have, at the interface between the adhesive and the UV-transparent substrate, the destruction of the outermost molecules, compromising the adhesion. Radiation indeed leads to the scission of polymer chains, which results in weakening and embrittlement of the bond. For instance, unsaturated polyesters are thermosets with a good radiation resistance, especially if charged with mineral fillers. Also cross-linked polyurethanes do not show any change in mechanical properties after exposure.

1.3.5 Plasticizer migration

Many thermoplastics can be solved in organic solvents, also called plasticisers, which are contained in lots of adhesives, even if in small quantities. The diffusion of these products inside the adhesive can soften it at the interface with the adherend and a possible stress on the joint may make the bond failing. Since diffusion is a slow process, this damage can manifest itself even after months. So surface pretreatment is fundamental for optimal adhesion during the lifespan of the joint, [24].
Other possible degradation causes are excessive mechanical stresses, that can damage the bonded joint in an irreversible way, or presence of biological organisms, which are attracted by certain kinds of adhesives.

1.4   Durability tests

Adhesive joint testing is needed to check the reliability of any bonded system. The reasons why these tests are carried out are several, going from materials selection, data acquisition for design purposes, validation and quality control, to environmental durability assessment itself. The key point is to use the best method for getting the wanted information and of course to guarantee its repeatability.

Table 1.2: List of all the technical characteristics that may be measured on adhesives [11]

Category	Measurable characteristics
Before use	Rheology and viscosity, consistency, thixotropy
	pH
	Solids content, ash content
	Specific gravity
	QC analysis: UV, IR spectra, chromatography, DSC, thermogravimetry
	Acid value, epoxy equivalent, hydroxyl value, isocyanate value
Characteristics of use	Viscosity and rheology
	Wettability (interfacial tension, critical surface energy)
	Working temperature, min. film forming temperature
	Mixing ratio of two components A and S
	Modes of setting, curing, polymerisation, drying
	Pot life, gel time
	Ring and ball temperature
	Gap-filling properties, thickness of joint
	Coverage or consumption
	Stability of the adhesive in the applicator's tank
	Sag resistance and flow
	Waiting time before assembly
	Tack
	Open time
	Pressure required
	Possibility of radiation curing (UV, EB)
	Setting time and setting speed
	Storage conditions and storage life
Mechanical properties of the	Adhesion to various substrates
	Tensile shear resistance
	Tensile resistance
	Peel strength
	Cleavage resistance, wedge test

(Continue from the previous page)

cured adhesive	Curve strain/stress, elongation at break
	Impact resistance and resiliency
	Creep under constant load
	Hardness
	Flexibility
Physical characteristics after curing	Elasticity modulus and flexibility, Poisson ratio
	Heat resistance, T_g, ring and ball temperature
	Cold resistance, brittleness
	Expansion coefficient
	Electrical c. (resistivity/conductivity, dielectric constant, loss angle, ionic purity)
	Optical c. (refraction index, light transmission)
	Vapour transmission, waterproofing
	Degassing under vacuum
Chemical characteristics	Resistance to water and humidity, corrosion, salt spray
	Resistance to oils, grease and plasticizers
	Resistance to chemicals
	Density of crosslinking
Other conditions	Fatigue resistance
Safety features	Flammability, flash point
	Toxicity, noxiousness
	VOC, environment position, exposure, threshold limits
	Allergic effects
	Formaldehyde content
	Contact with food
Cost	Price per kg, litre, m^2
	Specific gravity, coverage or consumption

There are both national and international standards that can be followed, but also industry and company specific ones are extensively applied. This happens because standard tests may not be necessarily the most appropriate in many cases: very often they can be used only in a qualitative or comparative way [5] and the possible properties to test are many, as exposed in Table 1.2.

The growing need to provide quantitative predictions of long-term performance, requires especially some properties of the adhesives, like modulus, strain to failure, yield stresses or fracture toughness. The most common applied tests are reported underneath, from [5].

Shear tests have different configurations, but in any case the shearing stress is obtained by applying a tensile load axially to the two lapped substrates. The

mean shear stress, τ, is measured, as the applied load divided by the area of the bonded overlap.
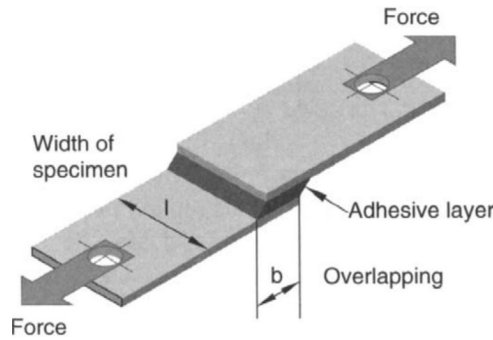
Figure 1.17: Single lap adhesive joint used in tensile-shear test [4].
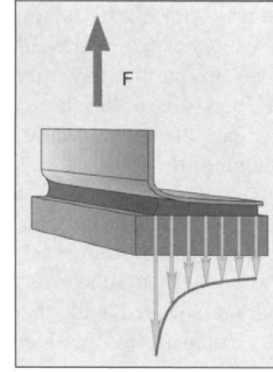
Figure 1.18: Stresses in an elastic-bonded adhesive joint subjected to a peeling force (F) [4].

Peel tests allow to assess the effects of processes or service on the strength of the adhesive/substrate interface, therefore at least one adherend must be flexible. The constant load per unit width is measured: it is useful to compare data, but not as well to provide quantitative measures of interface strength, because there is no guarantee that the fracture path will be along the interface.

Compressive tests reduce the risk of failure within the adhesive. However, no standard tests exist to measure the compressive properties of adhesives and little is known about behaviour beyond the elastic limit. Besides this, buckling of the sample can take place and it could be interpreted as yield.

Fatigue durability is checked, according to the adhesive final application, with a dynamic cyclic load, and data are plotted in the stress-cycle (Wöhler) diagram.

1.4.1 Artificial ageing

To improve lifetime prediction under service conditions, artificial weathering methods simulate the behaviour of the bonded adhesive under environmental influences like heat, cold, moisture, chemicals or UV-radiation and their combinations. In order to avoid tests lasting as long as the life expectancy of the product, accelerated (i.e. artificial) ageing is performed.

Polymeric adhesives are indeed viscoelastic, therefore the time–temperature superposition principle (TTSP) is widely used to predict their performances on different time scales than those experimentally accessible. This principle is based on the assumption that by increasing the temperature, the same molecular motions, that would occur more slowly at lower temperatures, accelerate [5].

Weathering chambers, made of a corrosion-resistant material, control all the necessary parameters (irradiance, temperature, humidity, salt spray).
The Arrhenius equation 1.1 is one of the best-known models for assessing the lifetime of polymers and is often used to predict the combined effects of temperature and time:

$$K(T) = A \ exp\left(-\frac{E}{RT}\right) \tag{1.1}$$

where, $K(T)$ is the reaction rate for the process (change of parameter with time), E is reaction energy, R is the gas constant, T is absolute temperature and A an empirically derived constant.

For what concern the physical aging (see section 1.3), Struik in 1969 demonstrated that its effect is to decrease the compliance of the material and that the short term aging curves can be related to each other by a shift factor along the time axis. Thanks to the TTSP (Time Temperature Superposition Principle) a master curve can be constructed, to have the effects of physical aging over extended times, with respect to those of the effective measurements.
Unfortunately, chemical aging cannot be related to only one model, being a complicated set of phenomena [2]. In this case the mechanical, thermal and chemical properties tested via accelerated aging are anyway converted into service conditions, through an acceleration factor, but the process can be hazardous. The effect of degradation in fact differs between materials and, even when considering the same material, among its properties a dissimilar degradation behaviour can be found. Finally, degradation mechanisms are sensitive to small changes in the controlling parameters and synergistic effects among degradation agents are hard to be recognized [5].

Chapter 2

Glues and and methods for aging characterization

2.1 Glues and substrates

The adhesives analyzed in this work are two different products by *PCS Innotec International N.V.*. The company provided the samples in two different colors, by which they are often referred: 'Black' for the **Versabond** glue and 'Grey' for the Adheseal one.

All the samples are prepared in a sandwich configuration, shown in Fig. 2.1: the glue is interposed between two substrates made of the same material. The substrates, also supplied by the company, are small squared panels and the area where the adhesive is deposited is of $4 \div 5$ cm^2. The materials possible substrates are five: ALW, BIT, EPDM, SIKA and TPO.
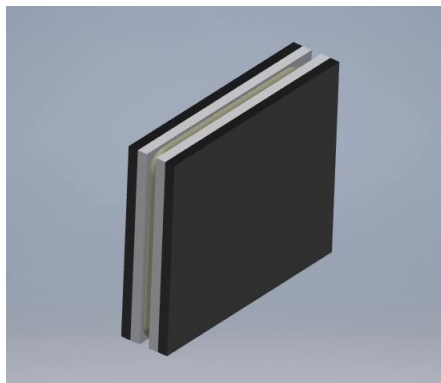
Figure 2.1: Reproduction of a standard sample: grey Adheseal glue bonds two substrates made of TPO.

2.1.1 Versabond
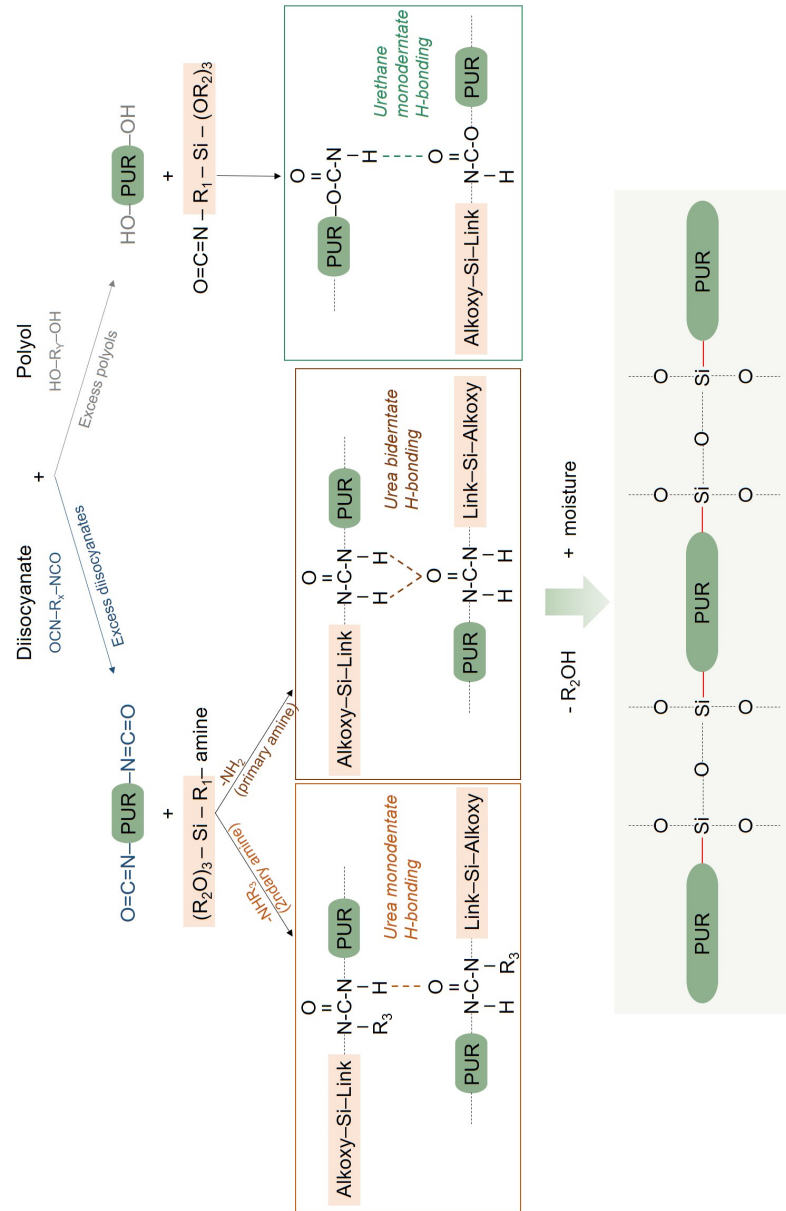
Figure 2.2: Schematic of the possible synthesis for SPUR, redrawn from [9].

Versabond is a SPUR, so a polyurethane terminated with silane groups. This technology shows many advantages: no solvents are contained, to avoid shrinkage or cracks after curing, neither silicones or isocyanates. This structure modification was introduced because the free isocyanate groups, present in traditional PURs, can provoke health concerns related to respiratory system and skin [25]. At the same time, polyether-based PUR exhibit a high water permeation, even though

they do not resist UV radiation [5].

In Fig. 2.2 a scheme is reported about the production of SPURs, from diisocyanates and polyols, to the possible prepolymers, which undergo hydrolysis and condensation to crosslink in presence of environmental moisture [9]. The bond between silicon and PU chain is made of urethane or urea groups, while the commonly used substituents are:

R_1: methylene, propylene or isobutyl

R_2: methyl or ethyl

R_3: aromatic or aliphatic

This glue is designed to work in the automotive and construction sector and adhere on nearly all kind of surfaces, like metals, concrete, stone, wood, PVC, EPDM, rubber. Moreover it can be used also in presence of moisture and water, such as in roofs. After drying, Versabond transforms into a tough, self-adhesive product [26].

2.1.2   Adheseal glue

Adheseal is a MS polymer, with a polyether backbone and silane terminal functionality. In [27] it is defined both as glue and sealant, thanks to its elasticity over a wide temperature range and its fast skin forming. Adheseal can be sprayed wet-on-wet and it is designed to be glued on several kind of surfaces, like metals, plastics, rubber, glass and Plexiglass. As well as the previous adhesive exposed, Adheseal does not contains solvents or isocyanates, but in this case urethane and urea are not present.

These construction sealants were firstly introduced in the market at the end of the '70s under the name of silyl-terminated polyether (STPE) [10]. The development of these polymers, which opened up a new market in the worldwide adhesives industry, allows to have nowadays all the necessary tools to design different MS polymer types depending on the specifications or properties required (Fig. 2.3).

The curing occurs in the presence of an appropriate catalyst, it is a fast double step process, illustrated in Fig. 2.4. The water present in the atmosphere reacts with the silane group of a methoxysilane, converting it into a silanol and liberating methanol. Further reaction of the silanol, with either another silanol or a methoxysilane, produces siloxane linkages and in turn methanol [28].
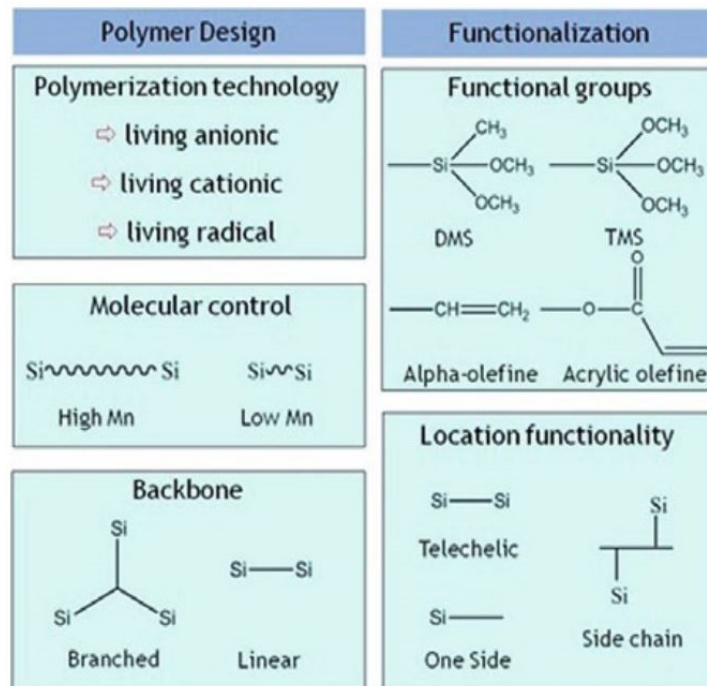
Figure 2.3: Useful features to design new MS Polymer technologies. DMS stands for Dimethoxymethylsilyl group, while TMS is the abbreviation of Trimethoxysilyl [10].
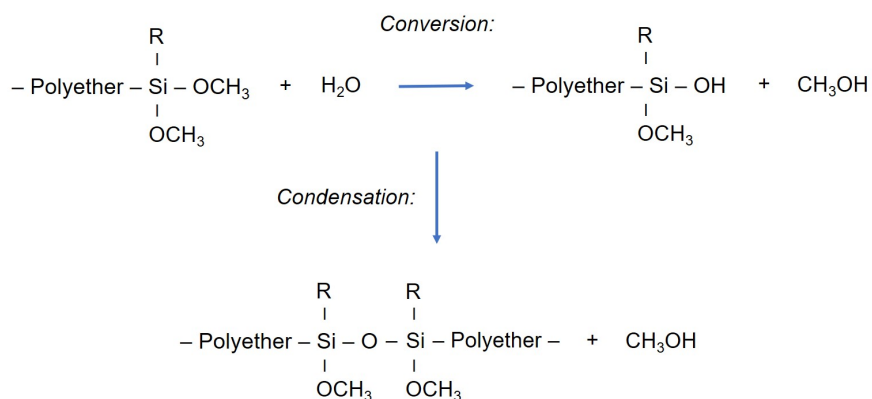
Figure 2.4: Adheseal crosslinking reactions.

2.1.3 Substrates

ALW It is a waterproofing membrane system for roofing or foundations application. The product consists of EVA and PVC, including some additives, such as mineral fire proofing, Ca/Zn stabiliser, epoxidised soybean oil, carbon black, titanium dioxide, pigments. The membranes are manufactured with a glass/polyester fleece backing in a calandering process. [29]

BIT *Elastomer bitumen* is produced by distillation of crude oil and refined by the incorporation of SBS polymers, to get a "rubbery" material that remains flexible even at low temperatures. Then a waterproofing reinforcement (Dörrkuplast® E-KV-4) is submerged in between two sheet of bitumen heat bonded mass, with a mopping method. [30]

EPDM *Ethylene Propylene Diene Monomer* rubber is a synthetic rubber, applied in vehicles seals and roofing membranes, since it does not pollute the run-off rainwater, even for extensive green roof systems, using lightweight vegetation. [31]

SIKA Sikaplan is a plasticized PVC, obtained adding phthalates to rigid *polyvinyl chloride* to make it more flexible and pliant. This flexible PVC in commonly used in buildings, such as in roofing membranes, resilient flooring, wall coverings, acoustical ceiling surfaces, waterproofing membranes and electrical cord insulation. [32]

TPO *Thermoplastic polyolefin*, also called olefinic thermoplastic elastomer, is a physical blend of a thermoplastic and an elastomer or rubber, with usually a filler. [33] TPO is commonly used on roofing applications because it does not degrade under solar UV radiation, but this material is extensively used in the automotive industry too. It has been formulated for long term weatherability, which is a requirement for roof overlays, replacement and new construction alike.

(a) ALW

(b) BIT

(c) EPDM

(d) PVC

(e) TPO
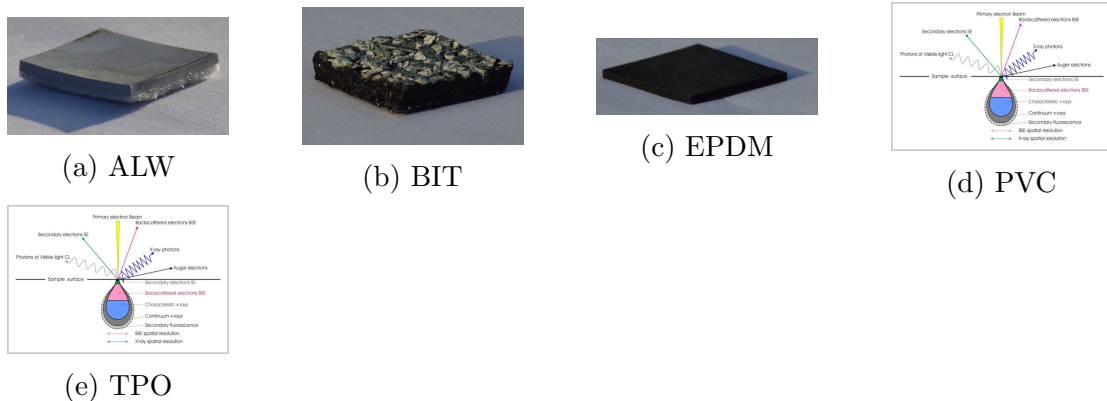
Figure 2.5: Substrates pictures: the upper side is the one in contact with the adhesive, in the inner side of the sandwich samples.

2.2 Methods for glue and aging characterization

2.2.1 Fourier Transform Infrared Spectroscopy

ATR-FTIR measurements are often used to monitor the progress of synthetic reactions, characterize the structure of prepolymers, but also of cured adhesives. Since in this work only cured samples are treated, FTIR is carried out to investigate the main composition of the glues and to compare the aged samples with the reference ones. In particular, it is possible to assign the peaks found in the spectra obtained with the functional groups present in the adhesives.

A GladiATR™ ATR from PIKE Technologies was installed on a Frontier Spectrometer by Perkin Elmer. Attenuated Total Reflection (ATR) is an infrared spectroscopy technique used to analyze surfaces or materials too thick or too absorbent to be studied in transmission.

$$d_p = \frac{\lambda}{2\pi n_p \sqrt{\sin^2 \theta - \frac{n_s^2}{n_p^2}}} \tag{2.1}$$

As shown by eq. 2.1, the depth of penetration (d_p) of the evanescent wave, but also the total number of reflections in the crystal, can be controlled either by changing the angle of incidence (θ) or by choosing crystals with different indexes of refraction (n_p). Since d_p is proportional to the IR radiation wavelenght (λ), the bands at higher λ are relatively more intense than those at smaller λ. In this project the transmittance was measured from 4000 cm^{-1} to 400 cm^{-1}.

Usually for strong absorbers or solid samples, as in this work, a small sampling area is used, called Single Bounce ATR. In chapter **??**, by comparing the results obtained with those from other works like [9] [19] [34], it is possible to define better the composition of the adhesives analyzed and to compare aged samples with the reference ones.

Figure 2.6: Schematic representation of infrared beam reflected on the crystal - sample interface in FTIR-ATR spectrometer.

Table 2.1: Exemple of functional groups in SPUR adhesives.

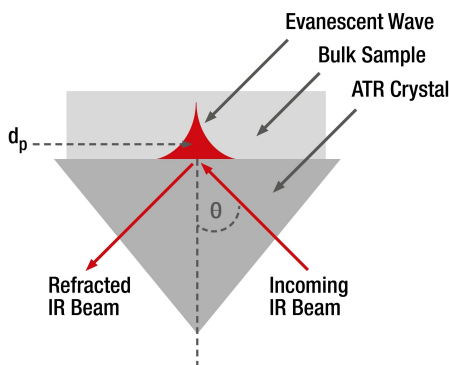| Notes	Functional Groups	Wavenumber [cm^{-1}]
	Urethane N-H stretching	3400–3300
I amide	Urethane C=O	1750–1700
	Urea C=O	1680–1600
II amide	N–H in-plane bending, C–N stretching	1600-1500
III amide	C–N stretching, N-H bending	1400-1200
	Si-OMe rocking	1194
	Siloxane multiple bonds	1127
	PPG C-O-C	1100
	Siloxane single bonds (Si–O–Si)	1060-1040
	Alkoxysilanes Si-OMe	2840, 1195, 1085, 863, 817, 774
	Silanol intermediates (Si–OH)	3700
	Residual NCO	2274
Residuals	Uncured Si–O–CH$_2$CH$_3$	960
	Methanol from hydrolysis	1035
	H$_2$O	3350, 720, 680

2.2.2 Scanning Electron Microscoppy

Thermal degradation can result in changes in morphological, mechanical and optical properties. So, with the aim of analyzing and comparing the microstructure of glue samples, SEM is carried out, to have easily a 3D imaging of the samples. A Phenom ProX SEM by Thermo Fisher Scientific was used. In Fig. 2.7a the basic structure of SEM is reported: the electrons are thermoionically produced and accelerated in a monochromatic beam. The magnetic lenses that are present reduce the beam size, to focus it before the interaction with the sample. Eventually the detector collects the signals and send them to a screen.

Must be said that only the inelastic scattering processes in Fig. 2.7b are collected from the detector, and among them two kinds are used in this work: BSD and SE. The first ones are electrons scattered at angles greater than π, originated in the surface '*diffusion*' layer. The SE are the result of the interaction between high energy incident electrons and valence electrons of atoms in the sample. Because of their low energy, only the secondary electrons very close to the surface can be ejected, this is the reason why the SE are very sensitive to topography.

Especially in case of non conductive samples as in this project, it is fundamental to avoid electrostatic charging of the surface analyzed, since the associated charge

instability can lead to unstable secondary emission, compromising the resolution and the image stability [35]. For this reason the samples were covered with an electrically conducting film (Au) as can be seen in Fig. 2.8.

(a) Schematic structure

(b) Representation of the beam-sample interaction
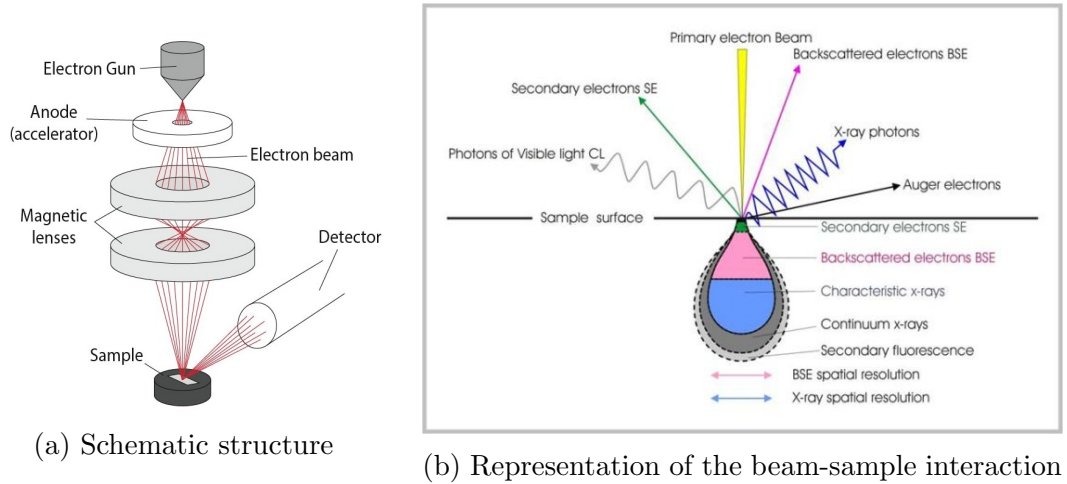
Figure 2.7: Scanning Electron Microscopy structure and interactions.
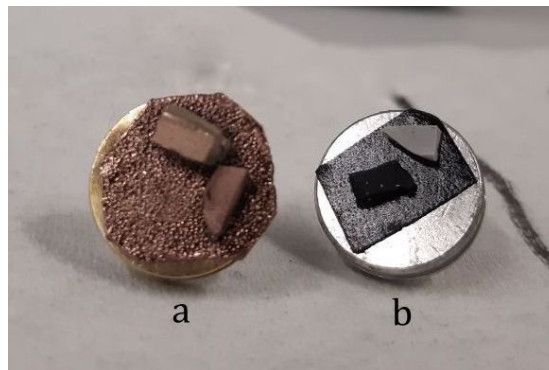
Figure 2.8: Glue prepared on the holder: a) two samples after gold sputtering and ready to be analyzed via SEM; b) two samples before gold sputtering.

2.2.3 Thermogravimetric analysis

TGA technique measures the amount and rate of change in the mass as a function of temperature. So, from the degradation temperatures recorded, the substances inside the sample may be determined. This implies that also water presence can be detected in the glue, thanks to changes in the weight loss around 100°C. The equipment used is TGA 4000 System by Perkin Elmer, run in a nitrogen atmosphere (flow of 20.0 ml/min). The temperature is increased from 35°C to

900°C at a rate of 20.00°C/min, in order to find out the degradation temperature of the glue and other deflections in its TGA curve that can contribute to the compositional analysis. Moreover also by comparing the results of reference and aged samples, eventually coupling them with those from FTIR, the functional groups of the evolved products during degradation can be identified [36].

2.2.4 Differential Scanning Calorimetry

In this calorimetric measurement, heat is supplied to or removed from the sample (with respect to a standard reference), during heating or cooling runs at constant speed. The material sample ($\sim 10\ mg$) is encapsulated in aluminum crucibles and kept in a controlled atmosphere. The general law to refer to is:

$$dQ = m\ c_p\ dT \tag{2.2}$$

where m expresses the mass of the sample and c_p its specific heat, the amount of heat that must be added to one unit of mass of the substance analyzed to cause an increase of one unit in its temperature.

It is know that by cooling, a polymer passes from the rubbery state to the glassy one, with an increase of the elastic modulus from values around the MPa to GPa. The temperature at which this occurs is called glass transition temperature or T_g, and it is a characteristic temperature for every polymer. It corresponds to a freezing of the macromolecular chains in a disordered state. As a consequence, from a rheological point of view, the viscosity of the polymer tends to infinity in the correspondence of the T_g.

In the DSC experiment transition associated to the T_g appears as a sigmoid endotherm discontinuity in the baseline. Its value is conventionally assumed as the temperature at half c_p jump or as the point of inflection of the curve. In polymerized adhesives, being the cure reaction completed, there is no more variation of the enthalpy except of the T_g [11].

DSC Q2000 by TA instruments was used, with a nitrogen flow of 50.0 ml/min. Two kind of test:

1. Temperature runs from 0°C to 250°C, to search for presence of water, any solvent or residual uncured fraction of material ;

2. Temperature ranges from -80°C to room temperature, to check the T_g and its possible variations with aging.

2.2.5 Dynamic Mechanical Thermal Analysis

In DMTA the material is subjected to a low amplitude periodic stress, the conservative-elastic (E') and dissipative-viscous (E'') components of the complex or dynamic

modulus (E^*) are determined:

$$E^* = E' + iE'' \qquad\qquad \tan(\delta) = \frac{E''}{E'} \qquad (2.3)$$

In which δ is the phase angle between input and output and the ratio, i.d. the relative importance, between loss (E'') and storage (E') storage moduli. Practically, the loss factor δ provides a measure of damping in the material. The glass transition temperature (T_g) can be determined since it corresponds to the maximum elastic dissipation: the storage modulus decreases suddenly and the loss modulus reaches a maximum.

DMA Q800 by TA Instruments is used in tension mode, because of samples' dimensions and clamps suitable for films, so for elastic but not sticky material as Adhseal after curing. The sample is placed between a fixed and movable clamp (see Fig. 2.9), with an oscillation amplitude of 10.0 μm, to avoid buckling. To check the T_g and its possible variations with aging, reference and aged samples are bought at -100.00 °C and kept at this temperature for a minute, then the data are recorded during a temperature ramp up to 30.00 °C, with a heating rate of 3.00 °C/min.
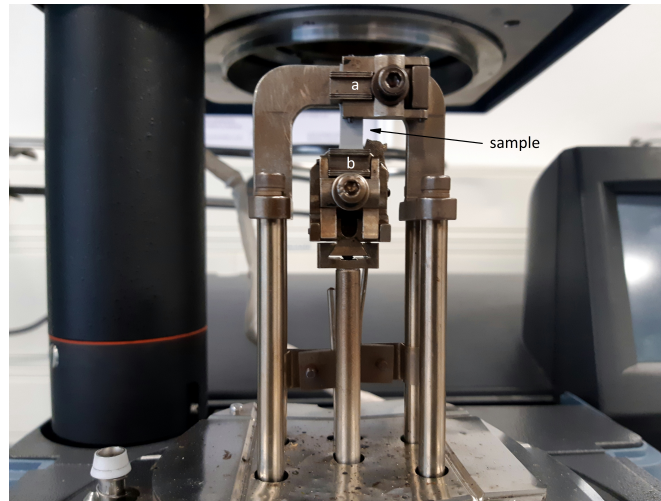
Figure 2.9: DMTA configuration: a) is the fixed clamp and b) the movable one.

2.2.6 Lap Shear test

To determine the durability of a joint, the shear strength is the critical mechanical property to investigate [23]. The *Lap Shear Rigid to Rigid test (ISO 4587)* is used with this aim: the tested piece is subjected to a shearing stress by applying a tensile load axially to the two lapped substrates. However, as described in section 2.1, the shape of the samples is not directly suitable for this kind of test. For this reason, a new configuration is adopted to test the shear strength of these

sandwich-like sample. As it is shown in Fig. 2.10a, the sample is stuck on a rigid PVC holder by means of a stiffer and more resistant glue[1] than the tested one. Due to the different shapes of the samples analyzed, the Lap Shear measurements have been recorded as Load [N] - Elongation [mm].
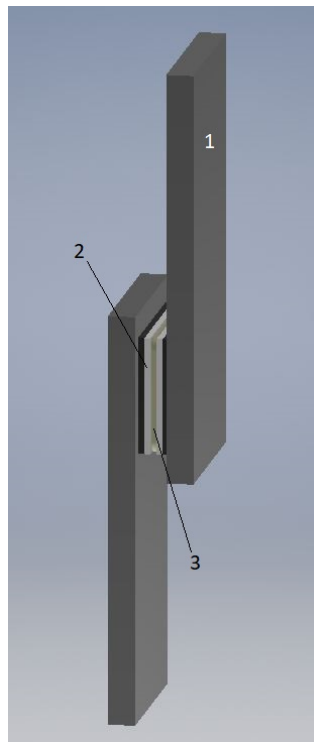
(a) Scheme of the sampling   (b) Real configuration used

Figure 2.10: Lap shear test.
1) PVC support 2) substrate, in this case TPO is represented; 3) the tested-glue, here a sample of grey Adheseal glue is shown.

The Lap shear test values give only an indication of the strength of an adhesive, since they are strongly related to the geometry of the samples. However, this is a good technique to evaluate the mechanical resistance of the bond. In particular, if the failure is adhesive, the failure is a result of the poor interfacial strength of the joint, and therefore the breaking load estimates the adhesion to the substrate, see Fig. 2.11. In case of cohesive failure, when the bulk mechanical properties of the polymer are predominant, the breaking load gives the internal strength of the cured adhesive [11].

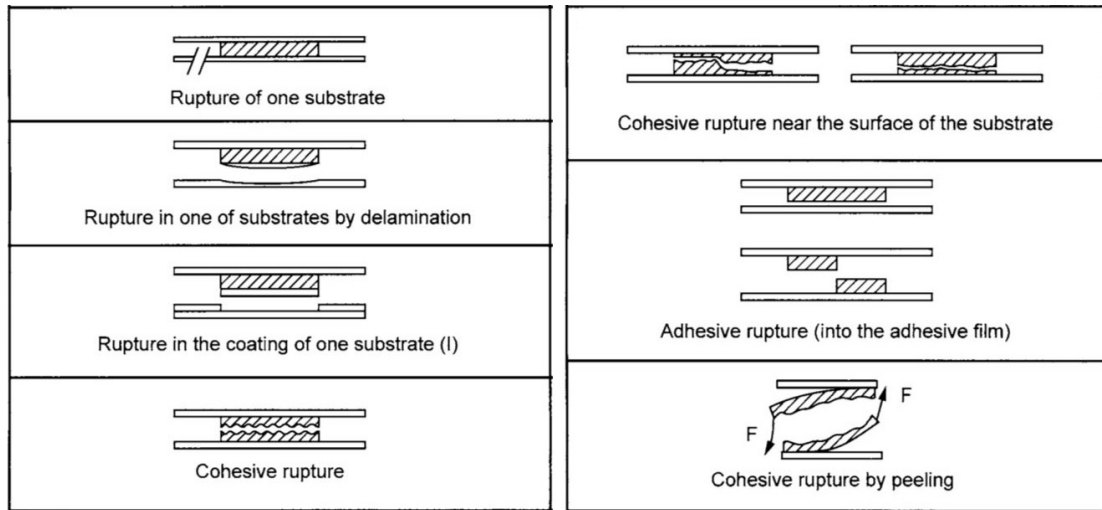[1]Metal Weld, provided by *PCS Innotec* too, see table A.1 in Appendix A

Figure 2.11: Modes of ruptures in adhesive joints [11].

2.2.7 Water absorption

This measurement is carried out to quantify the amount of water that can be absorbed during aging in submerged condition from Adheseal. Twelve samples are prepared, pouring the adhesive on a Teflon[2] substrate. Thanks to its non-sticking properties, the square specimens are easily removed from the substrate after curing, ready to be aged "alone", so without the presence of the sandwich structure used in the other methods.

The initial dimensions and weight are reported in Table 2.2, to be compared at the end of the test (60 days) with the final values. The dimensions of the sample are monitored because the extent of swelling may be related to the changes in mechanical properties of aged polymers, especially if the adhesive swells at the interface with the substrate [5].

The effect of temperature on the water absorption in distilled water is investigated, comparing some glue samples stored in the oven (called O_x_x) at a temperature of 60°C and other samples stored at room temperature (named R_x_x).

A classical Fickian law is found when the water uptake is directly proportional to the square root of exposure time. This kind of diffusion commonly gives good prediction of the mass uptake and the diffusion coefficient (D) can be easily calculated from the initial linear part of the sorption curve, that is where $\frac{M(t)}{M_\infty} \leq 0.5$. Equation 2.4 reports this calculation, in which h [mm] is the sample thickness and t [s] the immersion time.

$$D = \frac{\pi}{16} \cdot \frac{h^2}{t} \left(\frac{M(t)}{M_\infty} \right)^2 \tag{2.4}$$

---

[2]Teflon is the commercial name of poly(1,1,2,2-tetrafluoroethylene) often called PTFE as well.

However in many polymers, with particular networks or in specific environmental conditions, non-Fickian diffusion occurs when the relaxation of the polymer influences the uptake behaviour [37], [38]. Therefore more complicated laws are employed:

- Two-phase nature sorption model (dual stage Fickian model)

- Two-phase moisture sorption model (Langmuir-type model)

- Time or concentration-dependent diffusivity model

In other cases, the diffusion requires a new *ad hoc* model to be described, for which several detailed tests must be performed, varying the temperature and the humidity used.

Table 2.2: Water absorption samples.

Name	Width [mm]	Height [mm]	Thickness [mm]	Initial weight [g]
O_A_S	11	12	1	0.6642
O_A_B	21	18	1.25	1.4163
O_B_S	8.8	9.5	1.433	0.5739
O_B_B	15.3	15.4	1.067	0.958
O_C_S	7.8	8.6	1	0.4187
O_C_B	14.7	13.5	1.25	0.9177
R_D_S	7.8	8.9	2	0.525
R_D_B	15.2	20.2	1	1.1841
R_E_S	10	11	1	0.6156
R_E_B	14	15	1	0.9248
R_F_S	9.5	10	0.75	0.5058
R_F_B	19.25	18.25	1	1.3281

2.3   Methods for degradation assessment

2.3.1   UV transmission test

UV rays can contribute to the degradation of polymers, even in case of adhesives: their surface can be damaged, which can be sufficient to lower the adhesion to the substrate [4]. To evaluate if the solar UV-degradation should be taken into account within this work, an UV-transmission test is carried out on the different substrates considered for this study. The reason of this is that if the substrates transmit the UV radiation to the adhesive, a source of these rays must be included in the accelerated aging chamber; in the opposite case, it is not necessary, being

not meaningful for the real application of these products. The complete names of the substrates can be found in the abbreviation list, but must be said that COV and DUN substrates are just tested in this phase and not in the rest of the work. The equipment used, in Fig. 2.12, is a system composed of:

- PX-2 by Ocean Optics, a pulsed Xenon light source, with output between 220 nm and 750 nm

- Spectrometer USB4000 by Ocean Optics

- Fiberglass connectors

- Sample holder
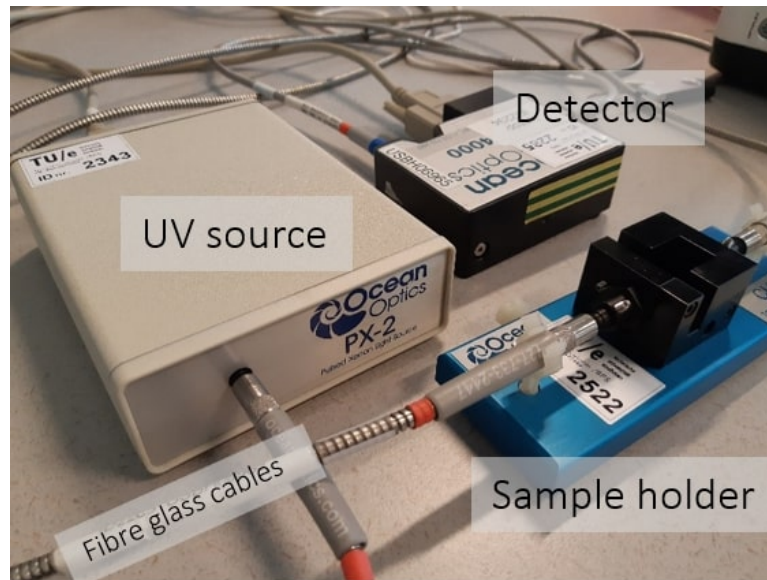
Figure 2.12: UV transmission test equipment.

2.3.2 Water presence simulation

As explained in the paragraph 1.3.1, water damages seriously the durability of adhesive bonds. Since the bonds may be subjected to water or humidity during their real application, the choice is to simulate both conditions:

1. 80% of Relative Humidity (RH)

2. Submersion in stagnant water.

This high level of relative humidity should overcome the critical RH, as exposed previously in 1.3.1. The aim is indeed to simulate the worst condition for the adhesive joint, together with immersion in water, which can happen for instance after long rain period in a roof application.

2.3.3   Accelerated aging

The samples are aged in a climate chamber (Memmert ICH750), kept at 80% RH, with the possibility to immerse some samples in the water. A temperature of 60°C is maintained, to accelerate the aging process without damaging the samples by exposing them at too high and unrealistic temperatures. Moreover the temperature chosen can be related to those that the adhesive must face during summer, especially on dark roof where the heat is absorbed and therefore transferred also to the adhesive beneath the protective panels.

The aging schedule is shown in Table 2.3, where all the labels used for the samples are reported. Reference samples are those just prepared in the sandwich configuration and stored at room temperature. They are sometimes referred as 'new' or '0 months' in the next chapters.

Table 2.3: Samples aging schedule

Name	Aging condition 80% RH		From (dd/mm/yy)	To (dd/mm/yy)
	Humidity	*Water*		
1m_water		×	27/06/19	29/07/19
2m	×		06/11/18	07/01/19
2m_water		×	27/06/19	22/08/19
3m	×		06/11/18	06/02/19
4m	×		"	07/03/19
5m	×		"	05/04/19
6m	×		"	07/05/19
7m	×		"	06/06/19
7m_water		×	"	"
8m	×		"	08/07/19
8m_water		×	"	"
9m	×		"	05/08/19
9m_water		×	"	"

Results

Chapter 3

Aging investigation

3.1 UV photodegradation

The results reported in Figure 3.1 report the part of the UV region related to the sunlight spectrum and. For all the substrates, the intensity transmitted is zero, so the UV rays will not affect for sure the glues, even in case of outside application.
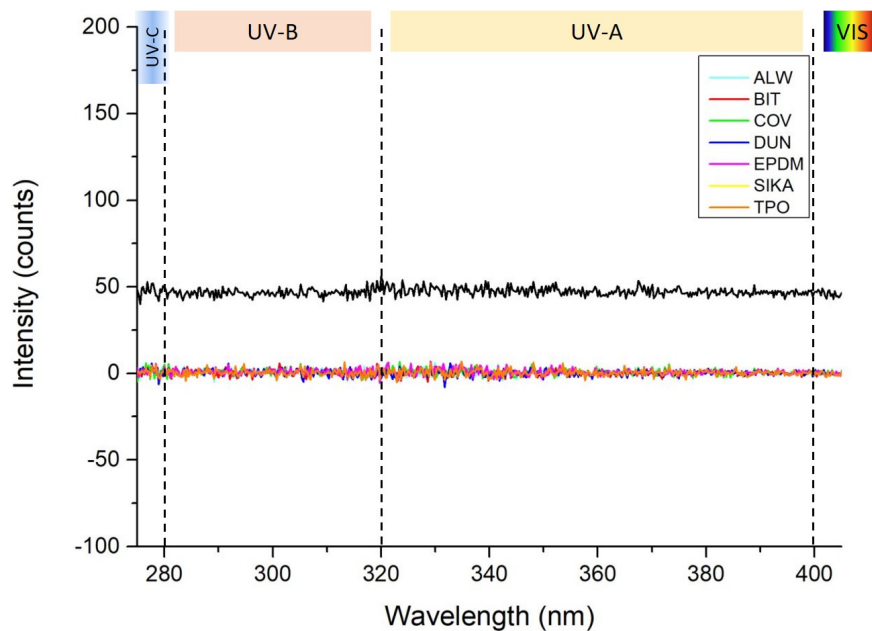
Figure 3.1: UV transmission analysis of the substrates

The black line reported in the graph is the signal recorded with no sample between the light source and the detector: the noise in this "background" line is due to the precision of the instrument. This explains why also the tested substrates do not show exact null intensity, but a noisy signal with oscillations of few counts.
It can be noticed that the UV-C region (100 ÷ 280 nm) is only partially reported in

this measurement. This is not a problem, because these rays are entirely screened out by stratospheric ozone at around 35 km altitude [39].

It must be added that the most sensitive wavelength window for polymer photodegradation is $280 \div 380$ nm, as in [40]. Therefore it is enough to consider only the UV-A and UV-B radiation, that reach the exposed surface of buildings, but not the adhesives at issue, which are completely protected by the substrates they bind.

3.2 FTIR

3.2.1 Aging in humidity

As Fig. 3.2 shows, Versabond is characterized by two main clear bands at 1730 cm^{-1}, due to the C=O in the urethane group. By aging, a small band is formed at 1562 cm^{-1}, which is related to N-H bending or C–N stretching. The labels present in the spectra graph are explained in Table 3.1, reporting their exact wavelength and the functional group they are associated to.
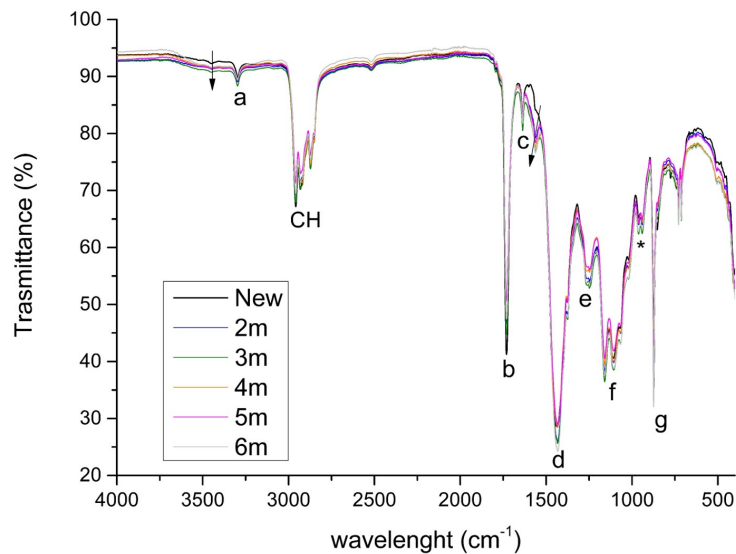

Figure 3.2: Comparison between the FTIR spectra of Versabond samples aged at 80% RH

Table 3.1: Functional groups found in Versabond.

Label	Functional Groups	Wavenumber [cm^{-1}]
a	Urethane N-H stretching	3297
CH	C-H stretching vibration	2960-2870
b	Urethane C=O	1730
c	Urea C=O	1636
d	O-H bending in carboxylic acid	1437
e	C–N stretching, N-H bending	1376, 1256
f	C-O stretching	1159-1069
g	C-H bending	874
After aging		
↓	H$_2$O	3350
↓	N–H in-plane bending, C–N stretching	1562
Uncured		
*	Si–O–CH$_2$CH$_3$	960

Adheseal spectrum, in Fig. 3.3, does not show meaningful changes, just two small peaks form between 1733 and 1640 cm^{-1}, pointed by an arrow.
Both types of glue show a small increase in the O-H stretch region (around 3360 cm^{-1}), due to the absorption of water in the material. Also in this case the peaks are reported in Table 3.2.
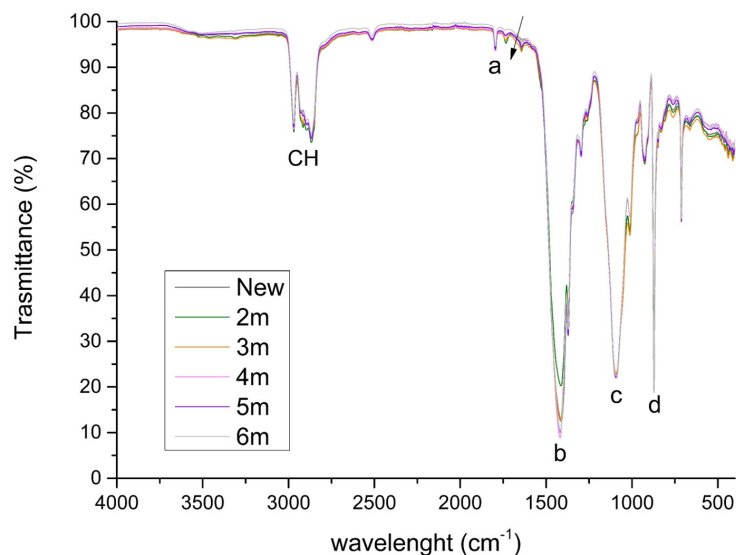

Figure 3.3: Comparison between the FTIR spectra of Adheseal samples aged at 80% RH

Table 3.2: Functional groups found in Adheseal.

Label	Functional Groups	Wavenumber [cm^{-1}]
CH	C-H stretching vibration	2970-2870
a	(rather small) C=O stretching	1796-1732
b	C-H bending in alkanes	1422 & 1372
c	C-O stretching in alkoxy group	1093
d	C-H bending	873
After aging		
$\downarrow$	H$_2$O	around 3350 & 1643

3.2.2 Aging in water

For what concerns the samples submersed in water, a certain amount of water penetrated in both the adhesive studied, according to the peaks appeared around 3380 and 680 cm^{-1} (see Fig. 3.4a and Fig. 3.4b). The peak at 1640 cm^{-1}, already found in humidity aged Adheseal samples, is more pronounced with this kind of aging. In both the graphs (Fig. 3.4), two aged samples are shown. '*6m*' stands for six months as explained in section 2.3.3, while '*5m+drying*' indicates that after five months of accelerated aging in water, the sample is kept out of the climatic chamber for twelve hours and then analyzed with the ATR-FTIR. This result is reported to demonstrate that water evaporates more easily in Adheseal with respect to Versabond, as if for the Grey glue a reversible mechanism of water penetration is involved.
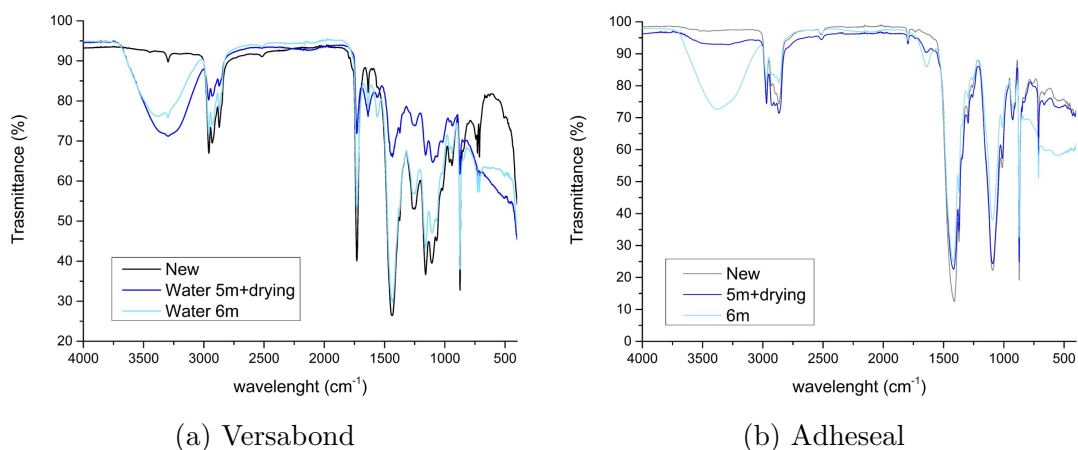

(a) Versabond   (b) Adheseal

Figure 3.4: Comparison between the FTIR spectra of samples aged in water

3.3 Microscopy imaging

Both the surface and the core of the two adhesives are investigated with the SEM, giving no overturned aging-related changes. There is the risk that the cutting process, to extract a proper amount of material for the microscopy purpose, may strongly modify the conformation of the cut part, compromising the pictures obtained.

3.3.1 Glue surface
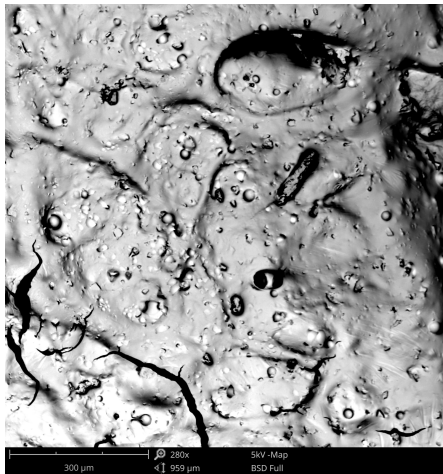
(a) reference, exposed surface
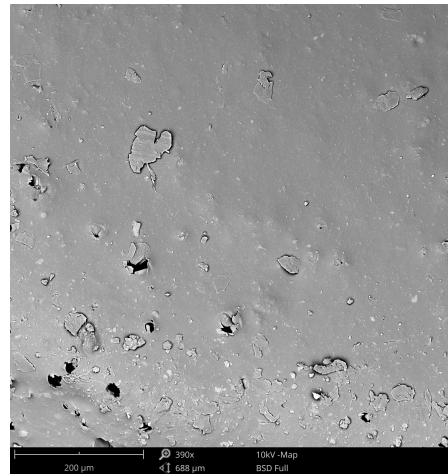
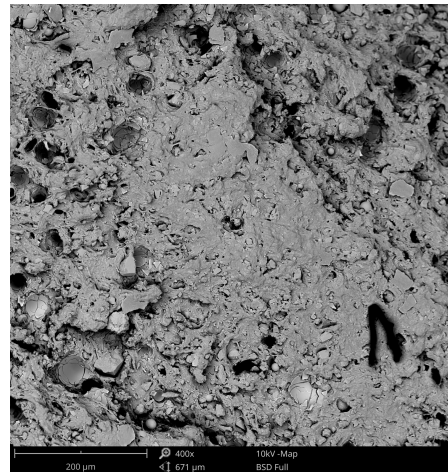(b) 4 months, exposed surface
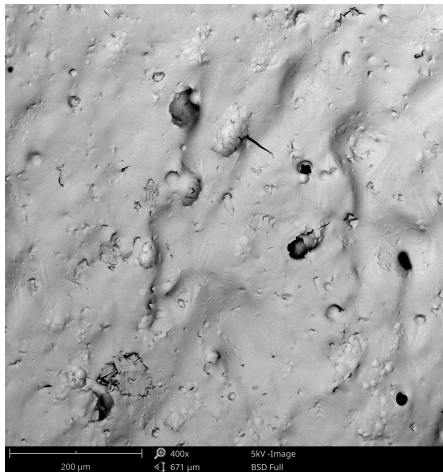
(c) reference, cut surface

(d) 4 months, cut surface

Figure 3.5: SEM pictures of Versabond, comparing the surface directly exposed to the environment with the one where the cut to extract the sample is performed.

Versabond is a very soft adhesive. In Fig. 3.5c, which shows the surface where the cut is performed, no scratches are present, due to the laboratory blade

action. Therefore Versabond does not seem to be damaged from the cutting process. Furthermore, no substantial differences can be found by comparing this image with Fig. 3.5a, which shows the surface of the sample as it is after curing (without being damaged from the sample preparation process). The plasticity of this glue is related to its capability to rearrange easily.

On the contrary, the surface of the same glue aged for four months is smoother (Fig. 3.5b) and, when this sample is cut to analyze its core (Fig. 3.5d), the glue seems really more damaged than in the previous case. This is also experienced by handling the glue to extract a small sample of it: Versabond seems to undergo a stiffening process, which will be discuss further in chapter 4.

For what concern Adheseal, a mild smoothing of the surface can be observed by comparing the aged samples with the reference ones, as if the glue recovers in a better way from the deformation caused by the cutting process, see Fig. 3.6.

(a) reference (b) 4 months
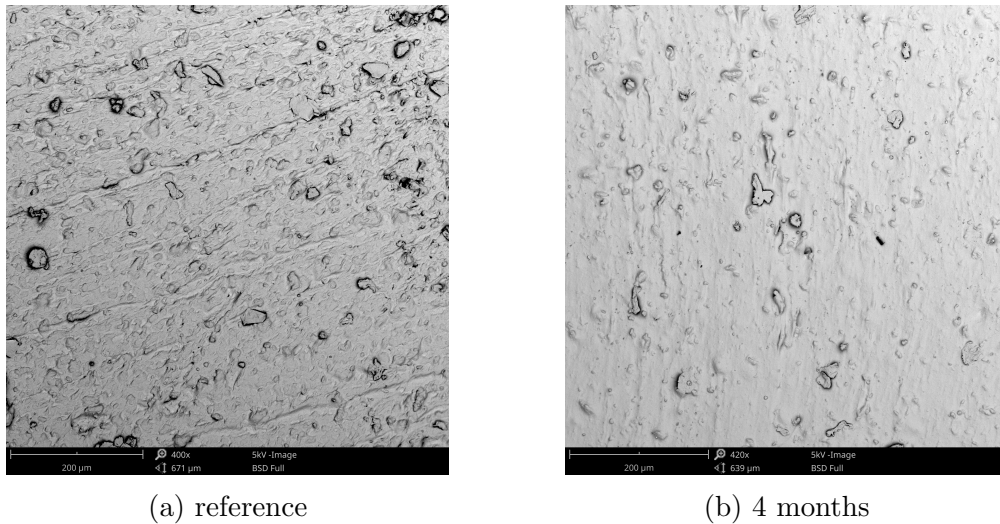
Figure 3.6: SEM pictures of Adheseal glue extracted from EPDM substrates

3.3.2 Interface

Observing Figs. 3.7 and 3.8 it is clear that the aging process has consequences on the adherence of the glue to the substrate. For both Adheseal and Versabond a sharper separation line between the adhesive and the adherend is found after the aging. As reported in section 1.3.1, for several types of adhesives/substrates, after exposure to humidity, water-rich layers are found at the interface. Water vapor penetrates between the substrate and the adhesive, decreasing their adhesion. These images show visually how this process takes place.

(a) reference

(b) 5 months
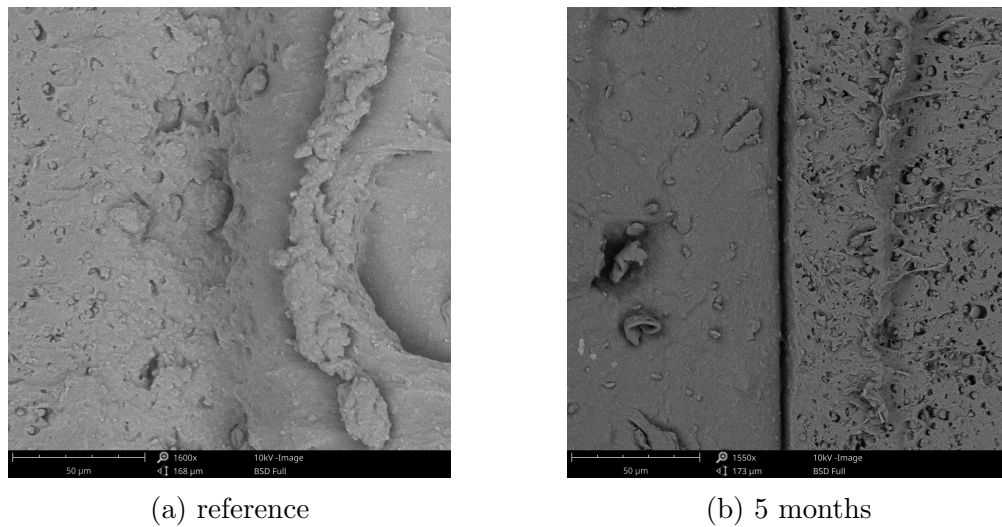
Figure 3.7: SEM pictures of the interface between Adheseal glue and ALW substrate

(a) reference

(b) 5 months
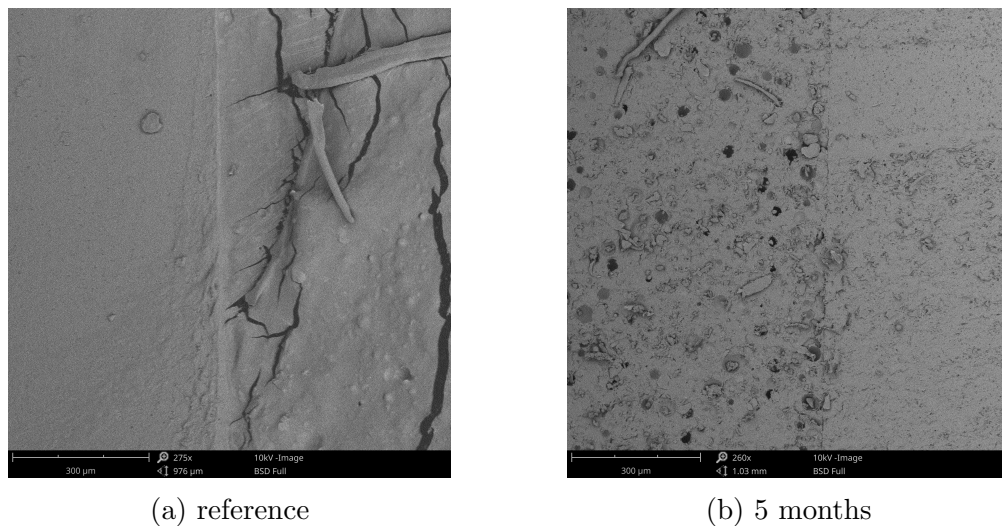
Figure 3.8: SEM pictures of the interface between Versabond glue and ALW substrate

3.4 Thermogravimetric analysis

This method of thermal analysis allows to check water presence in the aged glues through changes in the weight loss, in comparison with a reference sample. If present, also aging effects can be seen, correlated or not to water permeation. During aging, polymers can develop abnormalities in the chain, with consequences not only in mechanical properties, but also in the thermal behaviour [41]. In all the tests shown in Figure 3.9, both types of glue show a certain amount of inorganic

material inside, which is degraded after 700°C.

By aging in humidity (Figs. 3.9a and 3.9b) no noticeable changes are found. In the samples submerged during aging, the derivative plot DTG is shown (Figs. 3.9c and 3.9d). Water is absorbed by both types of glue, as shown by the peaks around 100°C, the boiling point of water. In particular on the surface of Adheseal water evaporates quite fast, while the water that has reached the core is trapped there.

(a) Versabond samples aged at 80% RH

(b) Adheseal samples aged at 80% RH

(c) Versabond samples aged in water

(d) Adheseal samples aged in water
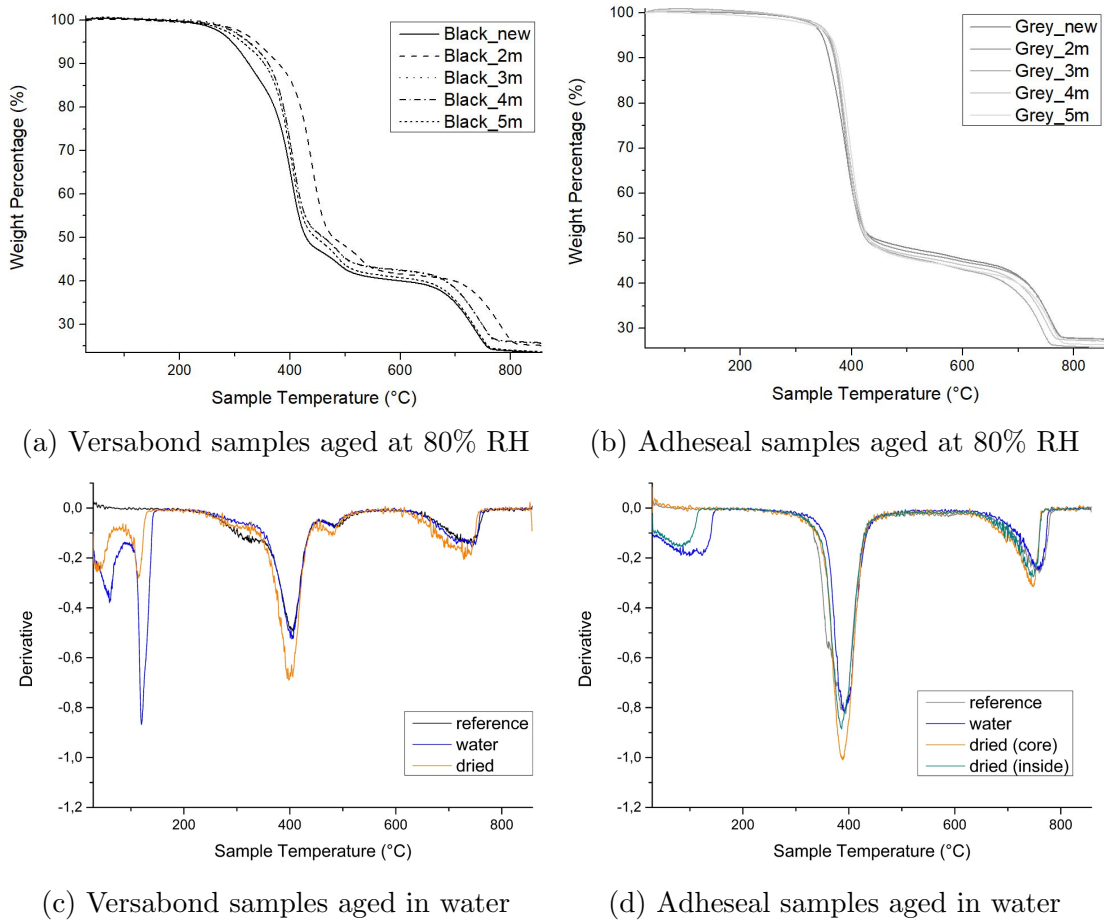
Figure 3.9: TGAs or the derivative plot (DTG) are reported for every materials and aging conditions considered

3.5 Differential Scanning Calorimetry

DSC test is performed to characterize the effect of water or vapor on the adhesive film. In fact, the presence of water in a polymer can have an effect on the glass transition temperature (T_g).

Firstly, the test is run from 0°C to 250°C, the results of Adheseal first cycle are reported in Fig. 3.10a. Since all the samples show a peak at high temperatures,

an unexpected effect of post-crosslinking is supposed. Therefore, in a sufficient period of time, heat exposition can increase the modulus of this adhesive, as a consequence of internal strenghtening [13].

Then another set of DSC measurements is carried out, in order to find the glass transition temperature of Versabond (for Adheseal, T_g is determined with DMTA, as shown in the next section) and its possible shifting with aging towards lower temperatures. This time, the temperature ranges from -80°C to room temperature: the glass transition temperature appears as a smeared transition in Fig. 3.10b, highlighted with a red bar: it is stable at -59.3°C for all the samples.

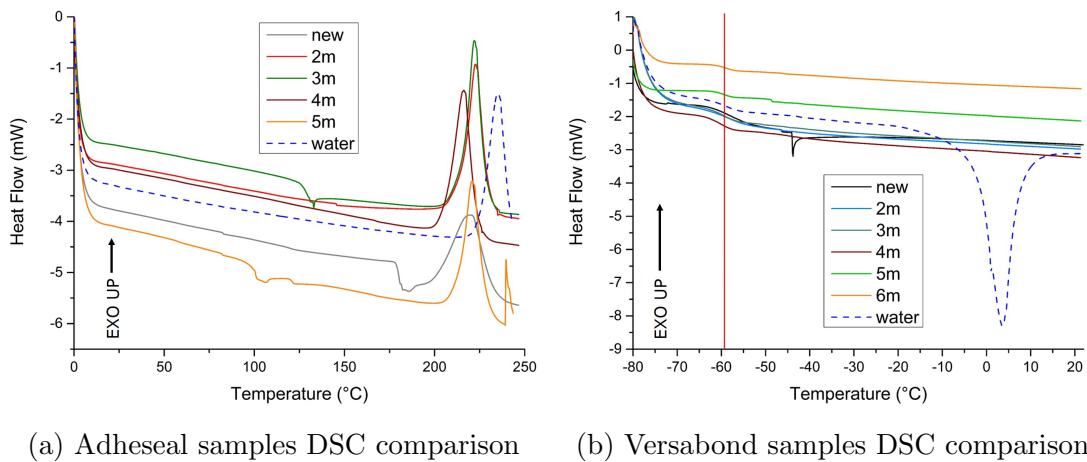(a) Adheseal samples DSC comparison   (b) Versabond samples DSC comparison

Figure 3.10: The calorimetries reported refer mainly to samples aged at 80% RH, but in both images one sample aged in water for six months is included

3.6 Dynamic Mechanical Thermal Analysis

As it is shown by Fig. 3.11, also for Adheseal there is no shift of the T_g due to the aging processes, it is stable at -49.6°C. However some differences among the samples can be noticed through the values reported in Table 3.3. The reference sample shows a storage modulus at -80°C lower with respect to the aged ones, as if they undergo a stiffening process. Observing the values of the storage modulus at room temperature, for what concerns the aging in humidity, there is an initial gain in stiffness, followed by a decrease when going on with the accelerated aging up to eight months. Instead the sample aged in water shows a loss in storage modulus at room temperature of 1 MPa, as if the glue has become more viscous because of water presence. These are really small differences, but if compared to the results shown in the next chapter 4, they anticipate what the lap shear test shows. As already said in the previous section 3.5, only Adheseal is studied by means of DMTA, because this technique is hard to apply to Versabond. For a very soft material like that, reaching low temperatures like -70°c implies to yield

or slip out of the clamp, invalidating the measurements.
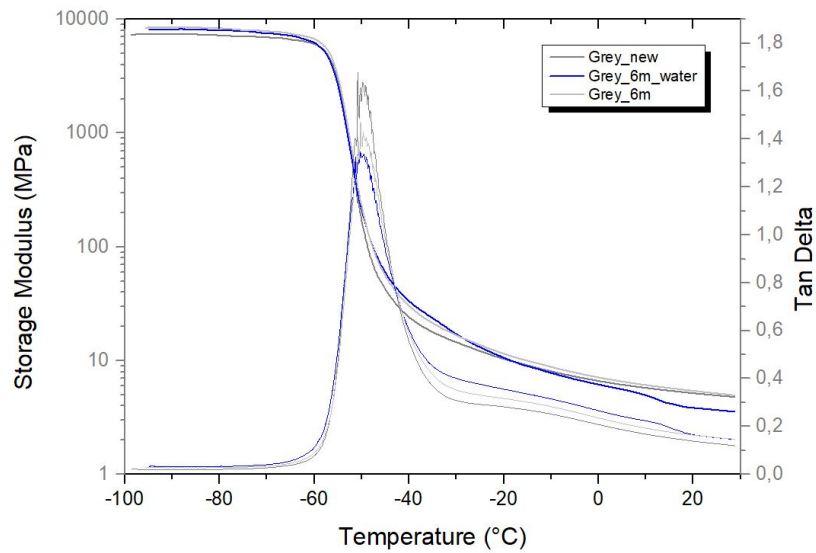
Figure 3.11: DMTA of the Adheseal glue samples: the storage modulus decrease of three orders of magnitude, in correspondence of the maximum of the $tan(\delta)$, which identifies the glass transition temperature.

Table 3.3: Values of storage modulus for Adheseal measured with DMTA

| | **Storage Modulus** [MPa] | |
Sample	at -80°C	at 25°C
reference	7238	4.9
6m	8373	5.2
6m water	8036	3.7
8m	8512	4.4

Chapter 4

Mechanical testing

4.1 Lap shear test results

The tested substrates with this method are BIT, SIKA, TPO and EPDM. No samples with ALW substrate can be included, as well as for the EPDM samples aged in humidity: detachment of the substrate from the PVC holders occurs before any failure regarding the adhesive. As anticipated in section 2.2.6, the adhesive bond can fail in different ways, reported in Fig. 4.1. The two failure categories are distinguished by using light or dark colors, according to the following legend:

● ● **adhesive**: when the glue is detached from one or both substrates;

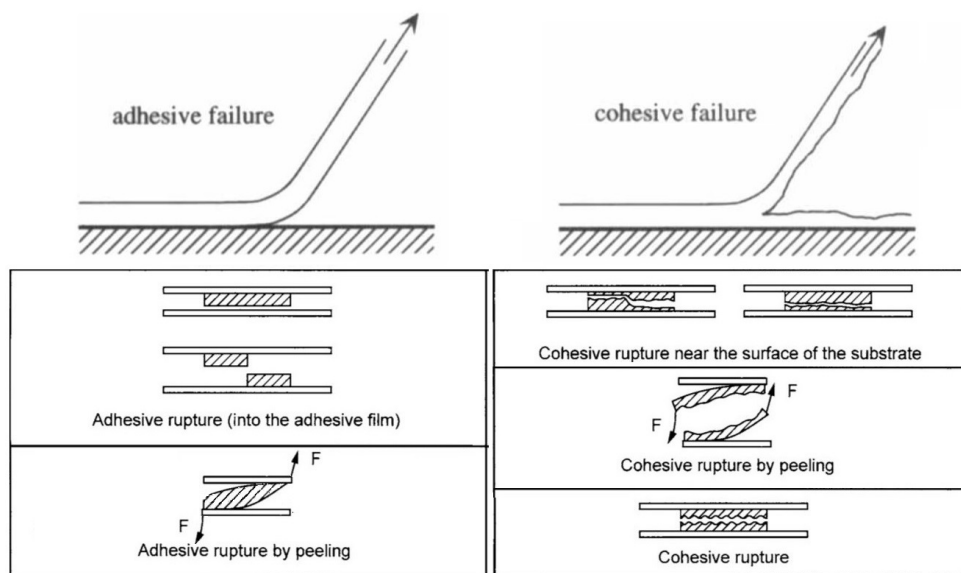● ● **cohesive**: when the value is related to the breaking of the glue itself.

Figure 4.1: Resume of the rupture modes actually found during the measurements, divided in adhesive and cohesive ones.

4.1.1   Aging in humidity

By aging in RH 80%, a common behavior can be noticed for Versabond samples, as in Fig. 4.2a, 4.2b and 4.3a. While at the beginning the reference samples are failing by breaking up, then all the aged ones detach from the substrate. Moreover the load needed to separate the adhesive from the substrate increases up to the sixth month, for then reducing in modulus. This behaviour corroborates what noticed in section 3.3.1: Versabond undergoes a stiffening process while aging.
An example of the curves obtained from the lap shear tests is shown in Fig. 4.3b. Two processes can be distinguished, as highlighted from the enumerated arrows:

1. The glue stiffens and starts to detach instead of breaking

2. The failure happens at the same extension (around 1 mm) but the load decreases.

(a) Versabond on BIT
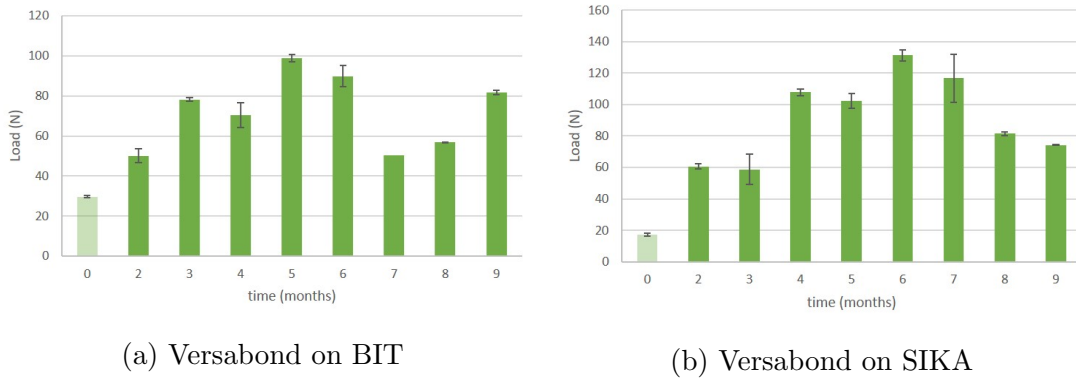
(b) Versabond on SIKA

Figure 4.2: Failure load for every month of aging in RH 80% - Versabond.

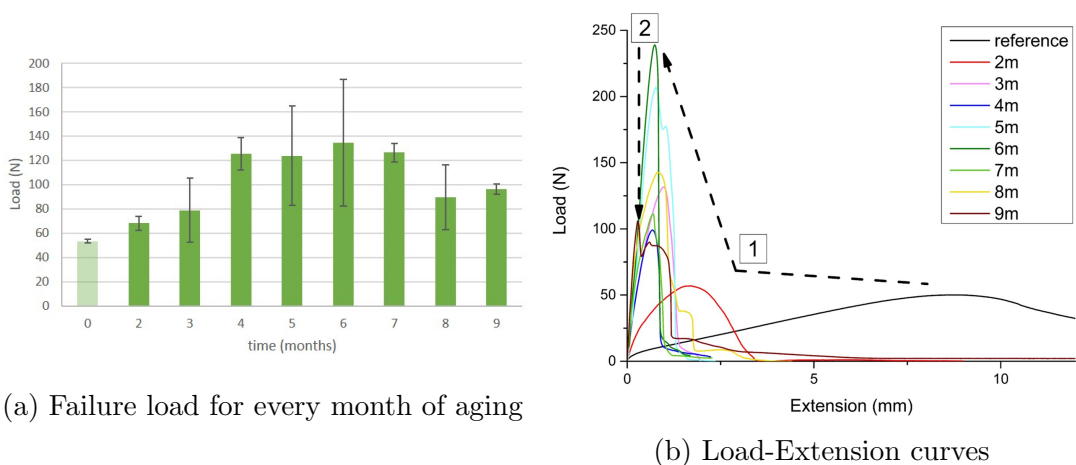(a) Failure load for every month of aging

(b) Load-Extension curves

Figure 4.3: Lap shear test results for Versabond on TPO substrate, comparison between reference value and samples aged in RH 80%.

As well as for Versabond, Adheseal glued on BIT, in Fig. 4.4a, registers an average increase of the failure load up to the sixth month of aging, and then a decrease follows. This is a confirm of what was observed during DMTA analysis of the Grey adhesive, in section 3.6, but also a possible explanation of the post-crosslinking peak found in DSC.

Only in the case of Adheseal glued on SIKA substrates the glue is always breaking up, with a drop in the failure load in Fig. 4.5a.

A similar reduction is present in Fig. 4.4b, although in this case the failure is by detachment.

Also for Adheseal an example of the curves obtained from the lap shear tests is reported in Fig. 4.5b, showing that the lowering of the breaking load is correlated with reduction in the extension achieved.

(a) Adheseal on BIT
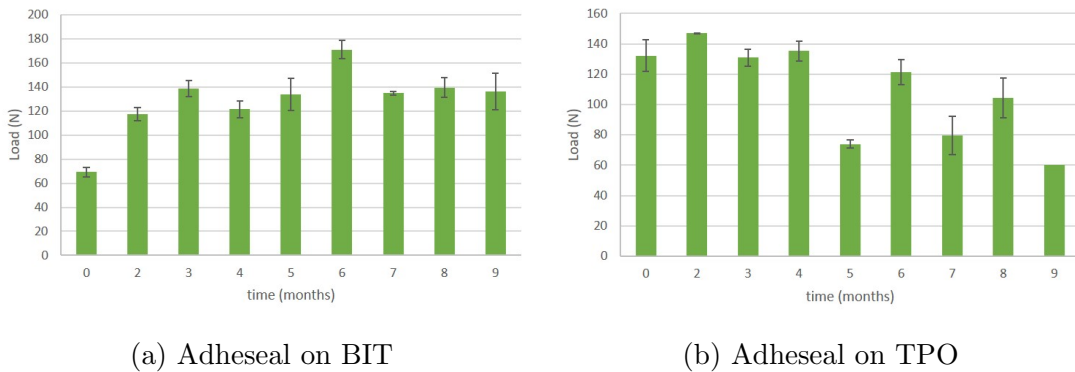
(b) Adheseal on TPO

Figure 4.4: Failure load for every month of aging in RH 80% - Adheseal.

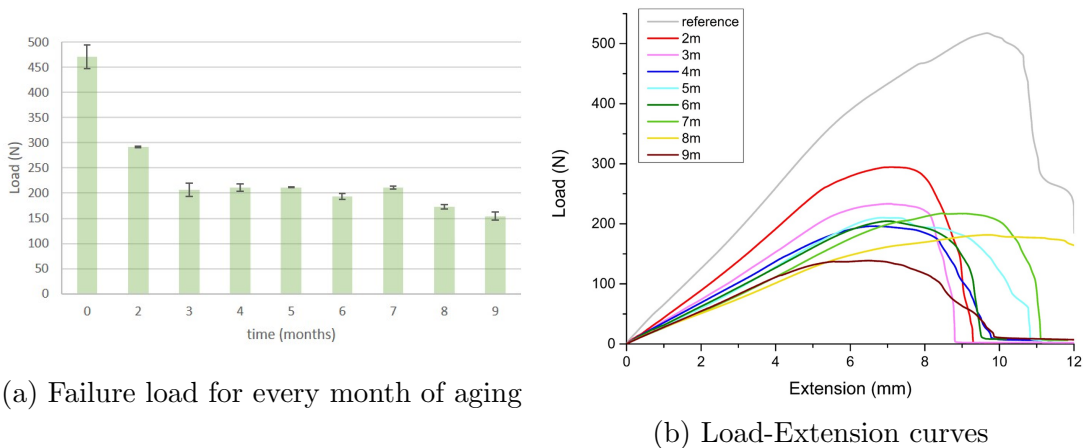(a) Failure load for every month of aging

(b) Load-Extension curves

Figure 4.5: Lap shear test results for Adheseal on SIKA substrates, comparison between reference value and samples aged in RH 80%.

4.1.2   Aging in water

For this kind of aging, only the data from the first two months and last ones (seventh, eighth, ninth) are available. However in this kind of aging, there is the possibility to test also samples with EPDM as a substrate. Unlike what happens by aging with 80% RH, where the EPDM substrate detaches from the PVC holder (showed in Fig. 2.10a), in the case of aging performed in water, the glue itself fails, either by rupture or detachment.

As well as for the aging in humidity, Versabond samples submersed in water (Fig. 4.6) show a change in failing mode, even after the first month in accelerated aging conditions. The reference samples break up, while the aged ones lose adhesion to the substrate.

Versabond is characterized by a double step behaviour similar to the one seen in RH 80% aging, even though the arrows in Fig. 4.8a highlight that the first tendency is a decrement in the load needed to break the adhesive layer. By going on with the aging, the detach mechanism takes over with also a progressive stiffening the glue. This behaviour is found not only in the case reported in figure, but also with the other substrates.

(a) Versabond on BIT

(b) Versabond on EPDM
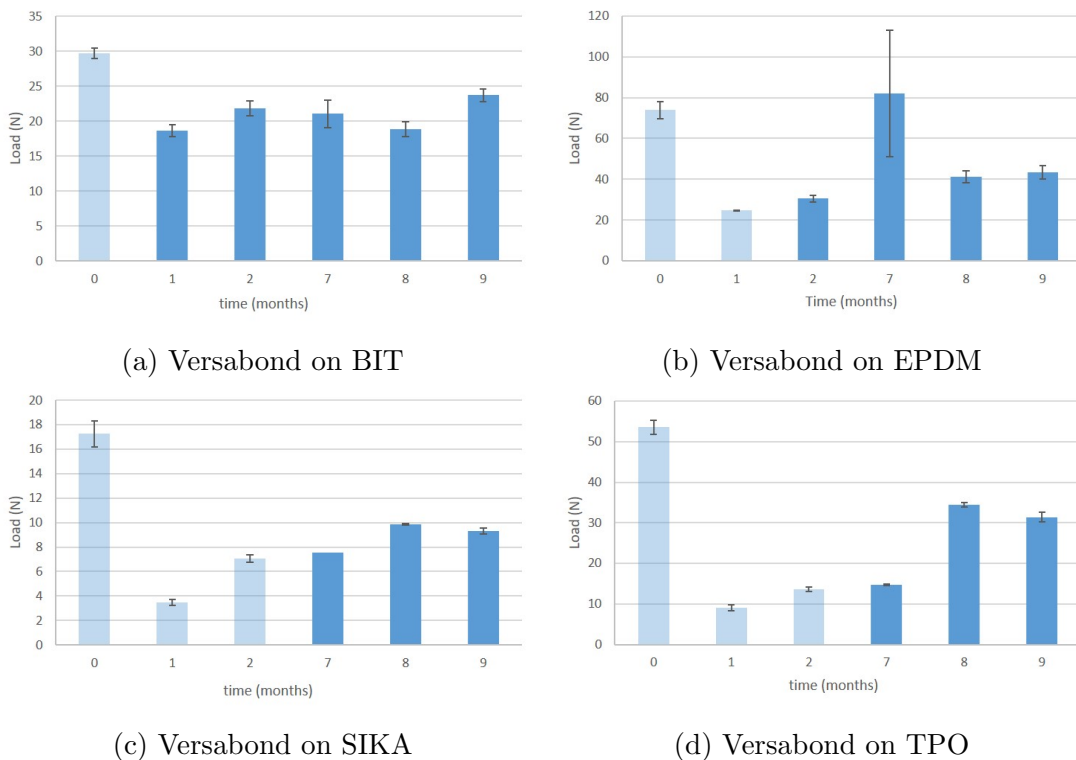
(c) Versabond on SIKA

(d) Versabond on TPO

Figure 4.6: Failure load for every month of aging in water - Versabond.

Concentrating on Adheseal glue behavior after water aging, a general decrease in failure load is found for all the substrates (see Figs. 4.7a, 4.7c and 4.7d), except for EPDM. In this case the reference value cannot be collected, as evinced from Fig. 4.7b, because the detachment from the support precedes the failure of the adhesive bond. However, the initial value for Adheseal on EPDM can be expected to be similar to the break-up-value of the reference sample on SIKA (in Fig. 4.5a), since the initial adhesion of Adheseal is optimal on both these substrates.

The curves load vs. extension in Fig. 4.8b confirm this trend, but a distinction must be done: when glued on BIT and TPO substrates, Adheseal detaches already in the reference specimens and, going on with the months, the load needed for the separation adhesive-adherend decreases. In case of EPDM and SIKA, at the beginning the adhesion is very strong and the only possible failure is cohesive fracture. For all the substrates at most from the first month of aging in water, the process taking place during lap shear tests is of adhesive nature, which is a quite surprising phenomenon in particular for SIKA. The values reached with this adherend and the complete change of mechanism suggest that the effect of the immersion in water is worse in this case than for the other substrates.
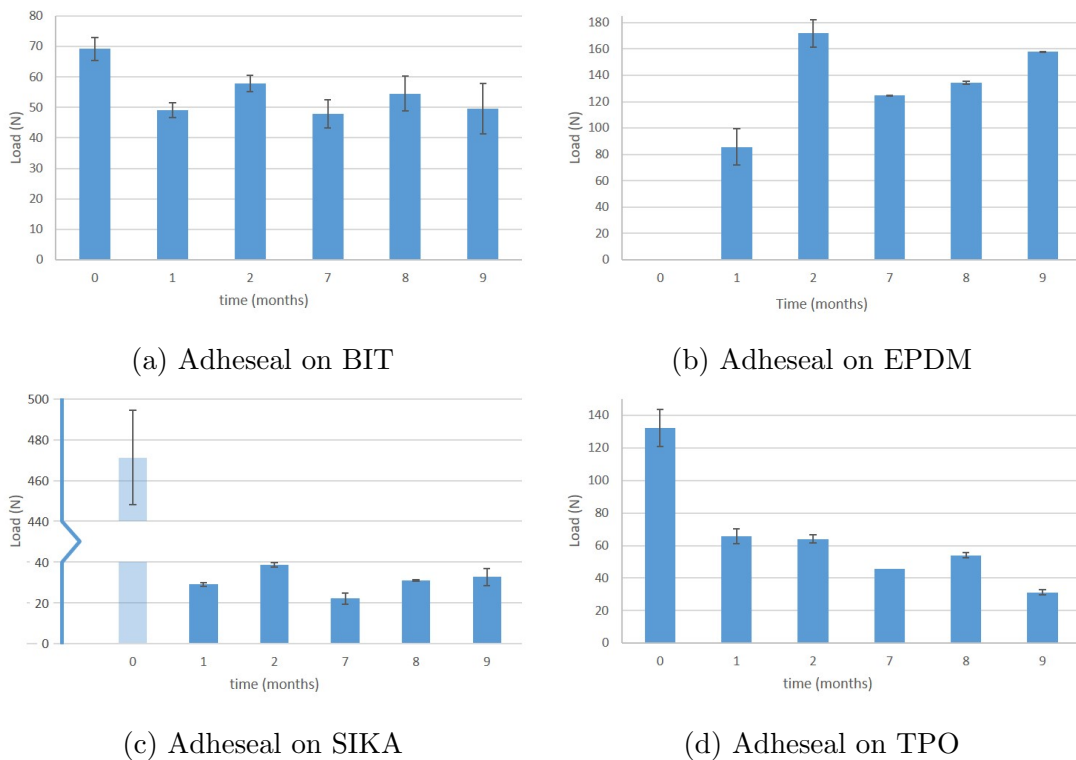

(a) Adheseal on BIT

(b) Adheseal on EPDM

(c) Adheseal on SIKA

(d) Adheseal on TPO

Figure 4.7: Failure load for every month of aging in water - Adheseal.

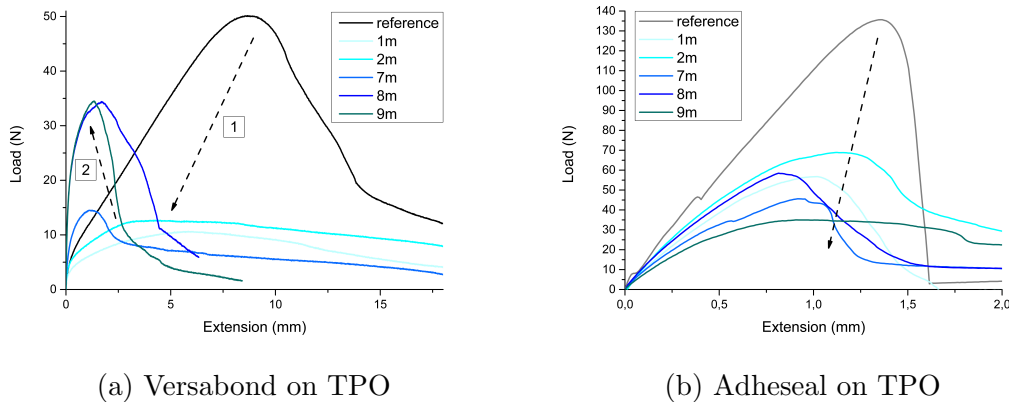(a) Versabond on TPO   (b) Adheseal on TPO

Figure 4.8: Load-Extension curves for Versabond samples aged in water, compared with the reference curve.

4.1.3 Comparison: Water vs 80% RH

In this section the general trends found in lap shear test results are exposed. Versabond, characterized by a soft and plastic nature, with cohesive failure, becomes a stiffer material, that undergoes adhesive detachment with both aging modes. However a different behaviour is observed between the two aging methods: for the humidity one, the load decreases only after the sixth month, for water submersion there is always a drop in the load borne from the first month of aging.

On the other hand, Adheseal demonstrates to be really dependent on the substrate where it is glued and aged. On the opposite of what happens for Adheseal on SIKA (see previous section), some common trends between the two aging modes are found, like for TPO. Nevertheless, the water effect is generally more drastic and with faster effects in time. Again Adheseal on SIKA can be taken as an example: aging in 80% relative humidity causes cohesive rupture up to the ninth month, whilst detachment takes place already since the first month of aging when submerged in water.
This tendency is likely due to the fact that 80% RH is still lower than the critical threshold of relative humidity, capable to decrease the joint resistance [42]. At low RHs in fact, the interfacial strength is higher than the cohesive strength of the bulk adhesive, so the joint failure occurrs entirely cohesively.
At higher humidity than the critical one, two phenomena contribute to reduce the external load necessary to induce the failure :

1. Moisture sorption produces swelling stresses;

2. Moisture attacks the interface itself.

The first contribution involve a set of compressive stresses near the edges and large tensile stresses in the center.

The second one takes place when the moisture content at the interface and decreases the effective contact area of the polymer with the substrate, weakening the interface [7].

To sum up, in this mechanical testing the set of all graphs obtained indicates that the behaviour of the adhesives studied is strongly dependent on the physical state and amount of water (80% RH or submerged) and the kind of adherend. This reliance of the results on the chemistry of the plastic adherend is confirmed in literature [2]. The migration of small molecules, such as plasticisers, stabilisers or catalysts, becomes important and can influence the strength of the adhesive or the quality of adhesion.

Chapter 5

Water absorption

5.1 Water absorption

An adhesive with industrial composition may have a non-classical behaviour in terms of water diffusion. The water absorption measurements are performed to check the diffusion behaviour of Adheseal.

The samples weighted have the whole surface exposed to water or moisture. Even if the accelerated aging condition reflects what can happen in real applications, it must be underlined this configuration and exposure of the adhesive are hardly faced in panel bonding, where the adhesive is always applied between surfaces to be bonded. This means that this test simulates the worst case, in which both panels do not shield the adhesive from water penetration at all.

The significant quantity to look at is the water uptake [%], that is calculated as in eq. 5.1.

$$Water\ uptake\ [\%] = \frac{wet\ weight\ [g] - initial\ weight\ [g]}{initial\ weight\ [g]} \cdot 100 \qquad (5.1)$$
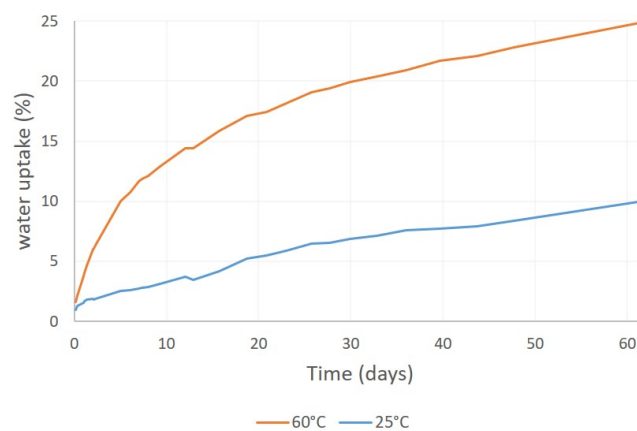

Figure 5.1: Water absorbed in time by the Adheseal glue samples.

Fig. 5.1 shows that in a period of 60 days the samples at 60°C show a water uptake of 24.9 %, while those aged at room temperature reach a *M(t)* of 10%. To investigate the absorption mechanism and compare it with the Fickian diffusion, the water uptake [%] vs. $\frac{\sqrt{time}}{thickness \cdot 10^6}$ $\left[\frac{\sqrt{s}}{m} \right]$ is plotted in Fig. 5.2.
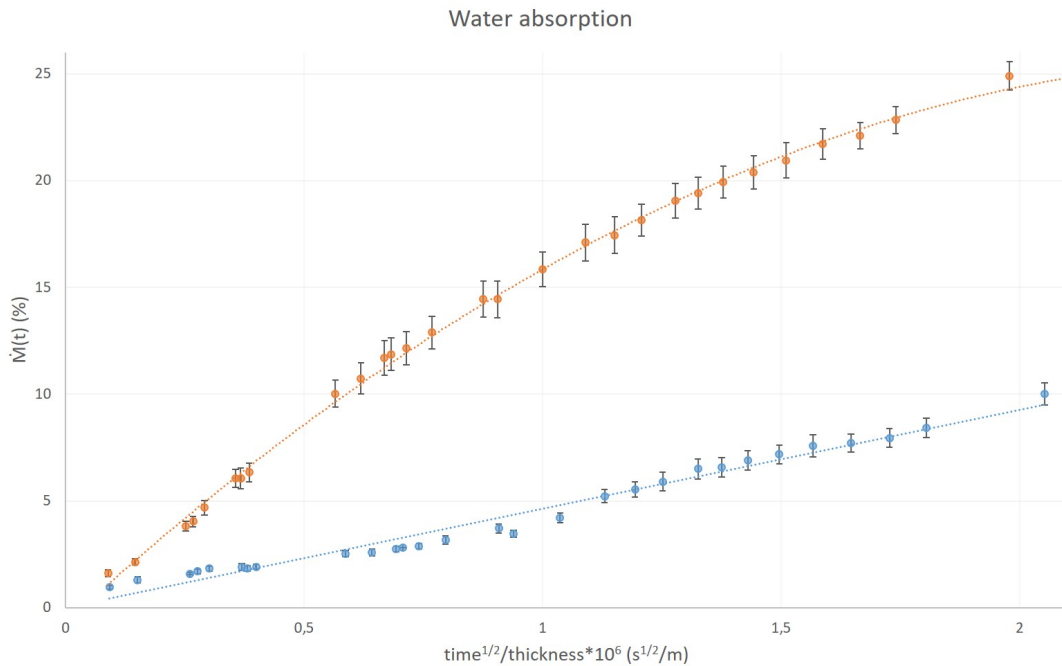

Figure 5.2: Water absorbed in time by the Adheseal glue samples: the water content is plotted as a function of the square root of time divided by the sample thickness.

For both temperatures, the plateau values of the water uptake as well as the initial slopes cannot be determined, preventing to calculate the diffusion coefficient. However it must be said that in literature examples of similar behaviours are reported, with no saturation after 50 days [38]. Among the reasons for this, there is the possibility that an increase of the absorption rate could also be attributed to the formation of voids or cavities.

Moreover it is demonstrated that adhesives may have a different behaviour according to the conditions they face. Usually non-Fickian diffusion is promoted by higher temperatures and higher relative humidity [16].

In particular if the mechanical relaxation rate exceeds the uptake, this last will increase linearly with time. This is what is observed for the measurements at 25°C, in which the points fit a linear tendency.

Concentrating then on the curve at 60°C, this behaviour can be related to the one exhibited by dual stage uptake. It belongs to the group of anomalous behaviours, where diffusion and relaxation have comparable rates. In particular it

is characterized by an initial Fickian diffusion, followed by a reduced uptake rate, and it finally reaches a saturation level at extended exposure times. This peculiar trend can be attributed to increased swelling and relaxation, particularly at high temperatures [43].

5.2 Swelling

Swelling is the volumetric change of an adhesive due to its absorbed moisture that becomes bound water, forming hydrogen bonds with the hydroxyl groups present in the polymer chains. Therefore the volumetric change in the adhesive is not proportional to the change in mass, which includes also the free water present. Finally swelling can create residual stresses, which may enhance furthermore water diffusion in an adhesive joint [16].

The increase in volume was measured after 47 days for all the samples used in the water absorption test. The values in fact reflect the results obtained in section 5.1: the samples exposed to 60°C show a more severe swelling, related to the higher amount of water absorbed, as reported in table 5.1.

Table 5.1: Percentage of increase in volume and thickness for the water absorption samples

Samples	ΔV [%]	Δt [%]
60°C	64.16	33.08
25°C	30.40	19.44

The increase in thickness is reported since, in both cases, it represents the largest contribution of the total volume increase.
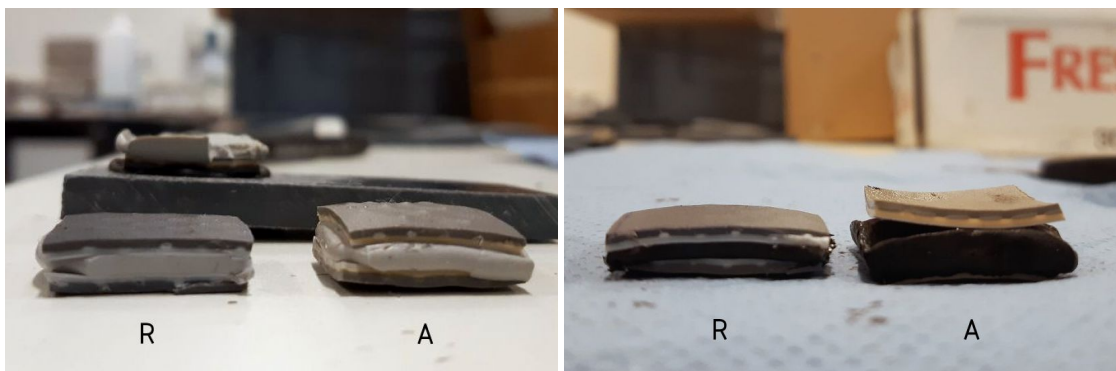
(a) Adheseal in SIKA

(b) Versabond in SIKA

Figure 5.3: Comparison between reference (R) and samples aged (A) in water

5.3   Water distribution at the interface

When water attacks an adhesive joint, the failure occurs usually near the interface. Therefore it is important to know not only how much water the adhesive absorbs, but also how the water is distributed throughout the bonded joint [5].

To show qualitatively how the water is more and more penetrating in time from the border to the center, four samples of Adheseal are glued, on one side, on the already used rigid PVC holder and, on the other, on a Teflon substrate, like the one used to prepare the samples for water absorption (see section 2.2.7). The sandwich-like adhesive joints are submerged in water at 60°C and analyzed respectively after 7, 20, 30 and 40 days.

The following pictures in Fig. 5.4 are taken immediately after detaching the specimens from the non-sticking Teflon substrate. The presence of water on the adhesive surface (i.e. adhesive/substrate interface) is highlighted with a chemical. The surface is sprinkled with a thin layer of anhydrous white copper sulphate (II), which reacts with water as in eq. 5.2:

$$CuSO_4(s) \; + \; 5H_2O(l) \; \rightleftharpoons \; CuSO_4 \cdot 5H_2O(s) \tag{5.2}$$

The hydrated copper(II) sulfate is characterized from a light blue color and it is easily noticeable on a dark substrate.

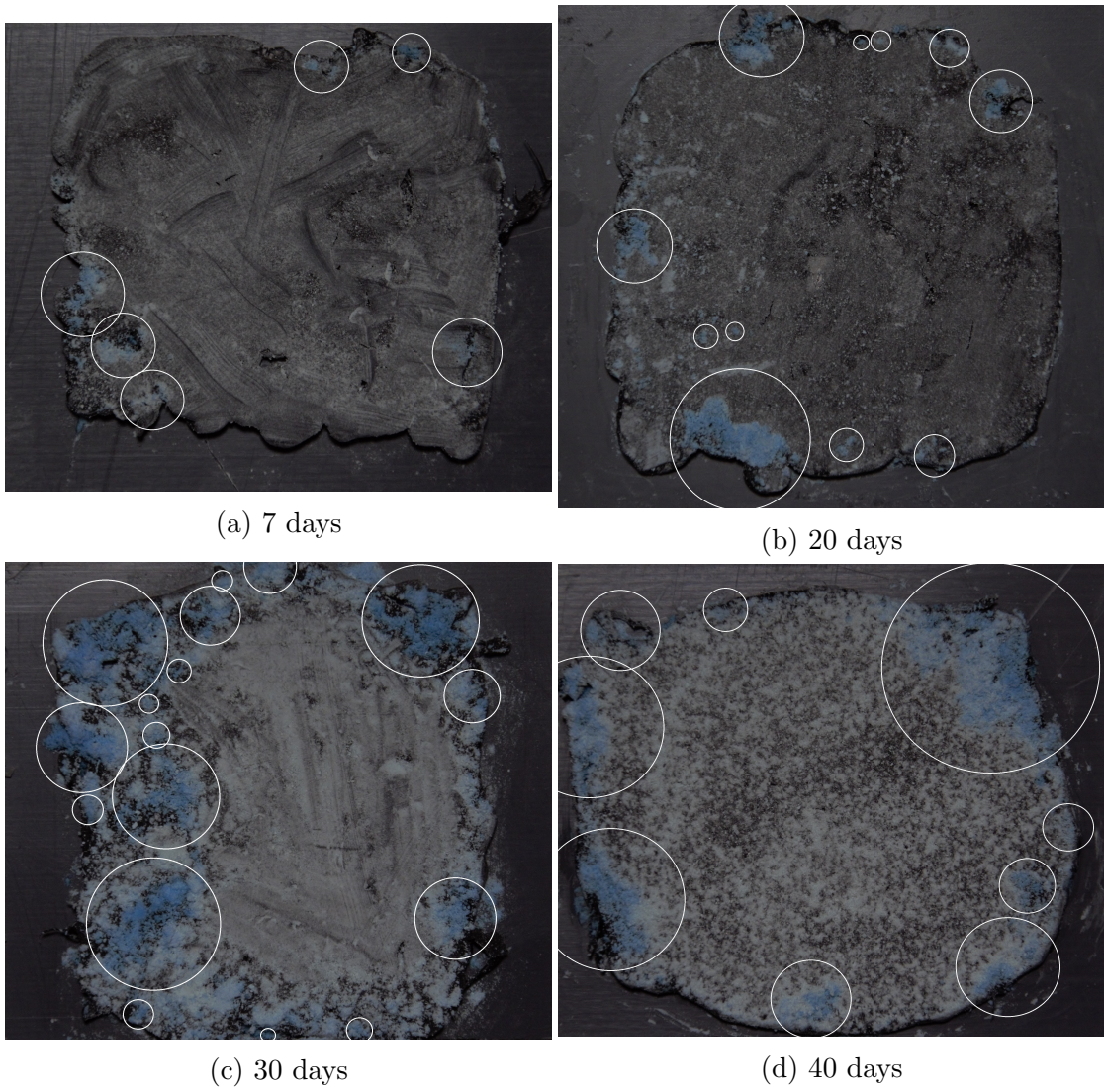In this way it is easy to visualize the water penetrating more and more at the interface by aging.

(a) 7 days

(b) 20 days

(c) 30 days

(d) 40 days

Figure 5.4: Adheseal glue interface after submersion in water at 60°C

Conclusions

For the considered adhesives, UV degradation cannot be found, since the substrates shield them from this harmful radiation.

From a chemical point of view, there are no relevant changes, even though water is always present, in larger amount in the samples submerged in water. In particular it is noticed that water infiltrate at the interface between the substrate and the glue.

Lap-shear test together with water absorption prove that the glue adhesion can be severally diminished by water, which penetrates in the glue and at the interface with the substrate, promoting the detachment of the glue from it.

Given the strong dependence of the results on the material, that constitutes the substrate, this work opens the door to study the role of plasticizers, which could explain the different kind of degradation found.

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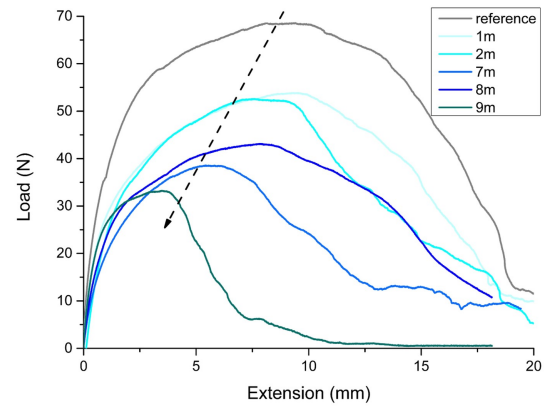
Appendix A

First appendix

Table A.1: Mechanical properties of *Adheseal* and *Metal weld*, from data sheet.

Property	Adheseal	Metal Weld
Tensile strength	2.60 N/mm^2	34 N/mm^2
Shear strength	1.70 N/mm^2	26 N/mm^2
Elongation at break	400%	5.5%
Hardness	55 (Shore A)	75 (Shore D)

Lap shear curves
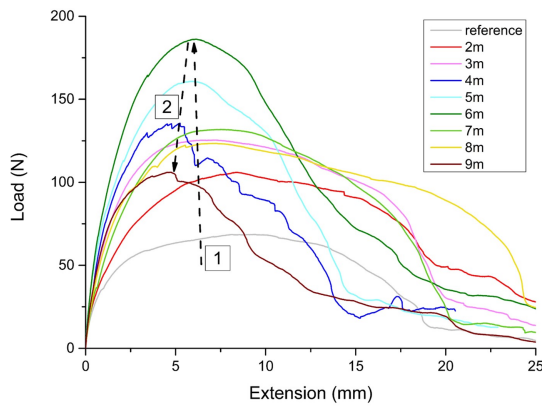
(a) Adheseal on BIT - humidity aging
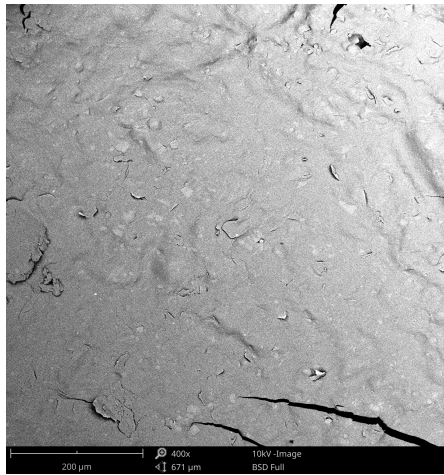
(b) Adheseal on BIT - water aging
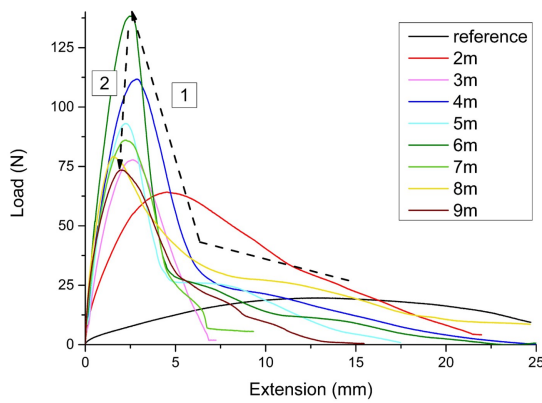
(c) Versabond on SIKA - humidity aging
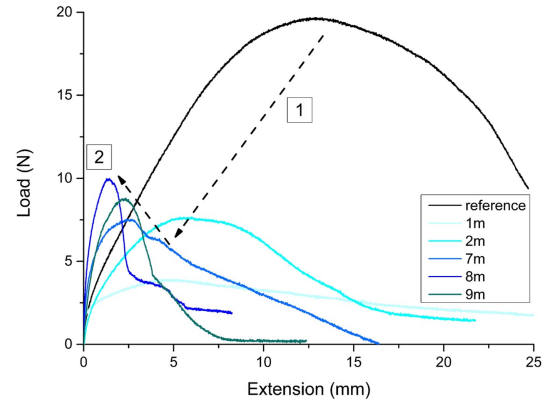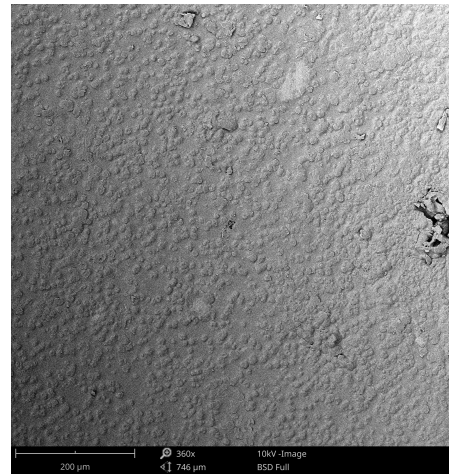
(d) Versabond on SIKA - water aging

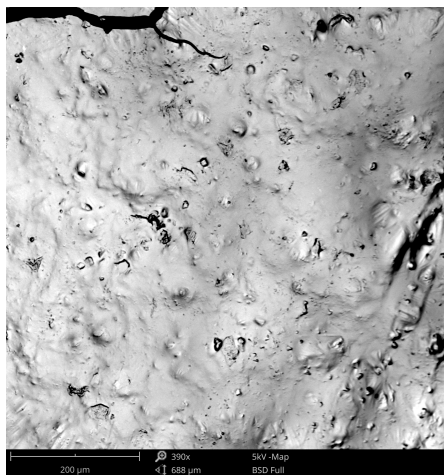Figure A.1: Load vs extension curves.
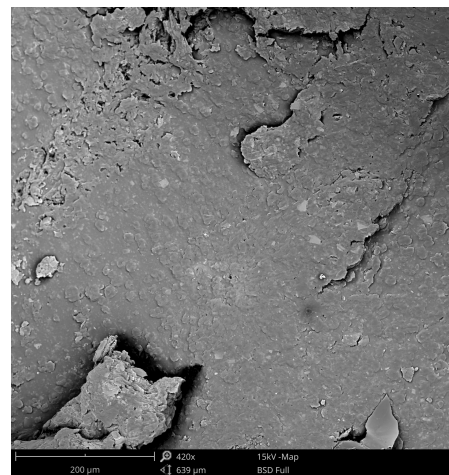
SEM

(a) reference

(b) 4 months

Figure A.2: SEM pictures of Versabond glue extracted from EPDM substrates

(a) reference

(b) 4 months

Figure A.3: SEM pictures of Versabond glue extracted from TPO substrates