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Management e Sicurezza delle Costruzioni

*“Sviluppo e sperimentazione di nano-reti in
PVB per l’ottimizzazione di vetri laminati”*

*“Development and testing of PVB nano-nets for the
optimization of laminated glass”*

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Abstract

The architectural and engineering trend leads towards greater use of glass in buildings. Growing safety awareness often requires laminated glass. Laminated glass is formed as a sandwich of two or more sheets of glass and a plastic interlayer. Laminated glass can for example be used in stairs, floors, facades and balcony railings.

This thesis deals with the most common interlayer material: polyvinyl butyral (PVB). Standard sheet of PVB has been widely studied with several researches; in this work, a new type of sheet form was characterized. PVB nano-net was analysed with several tests (i.e., *Water Absorption Test*, *Tensile Test*, *Single-Lap Shear Test*, *Ageing Test*, *Scanning Electron Microscope* and *UV-Vis Test*) and it was compared with standard sheet.

The main aim of the work was to evaluate if other PVB shapes than continuous film, for example nano-net, could led to better mechanical or thermo-physical properties for this material. Indeed, this improvement was demonstrated in literature for other types of supports (for example laminated phenolic composites).

Several mechanical and thermo-physical experimental tests allowed demonstrating that the nano-net brings improvements compared to the standard PVB only on energy aspects while determines some drawbacks as regard mechanical issues. Indeed, it determines:

- Greater water absorption, which could lead to delamination phenomena of the laminated glass;
- A reduction in elongation and in the relative ultimate tensile strength at failure but with an increase in the toughness of the material (three fundamental parameters that influence the global behavior of laminated glass);
- A reduction in the adhesion capacity between glass and plastic interlayer with consequent loss of performance of the structure;
- Slight loss in visible light transmittance, but a significant improvement in the solar radiation range.

Sommario

La tendenza architettonica e ingegneristica porta verso un maggiore utilizzo del vetro negli edifici. La crescente consapevolezza della sicurezza richiede spesso il vetro laminato. Il vetro laminato è formato da un sandwich di due o più lastre di vetro e uno strato intermedio di plastica. Il vetro laminato può essere utilizzato ad esempio in scale, pavimenti, facciate e ringhiere di balconi.

Questa tesi tratta il materiale intercalare più comune: il polivinilbutirrale (PVB). Il PVB standard è stato ampiamente studiato con diverse ricerche; in questo lavoro è stata caratterizzata una nuova forma di foglio. Il PVB nano-rete è stato analizzato con diversi test (es. *Assorbimento d'Acqua*, *Test a Trazione*, *Test ad Adesione*, *Invecchiamento*, *Scanning Electron Microscope* e *Spettrofotometria*) e, i risultati, sono stati confrontati con il foglio standard.

L'obiettivo principale del lavoro era valutare se altre forme di PVB oltre al film continuo, ad esempio nano-reti, potessero portare a migliori proprietà meccaniche o termo-fisiche per questo materiale. Tale miglioramento è stato infatti dimostrato in letteratura per altri tipi di supporti (ad esempio compositi fenolici laminati).

Numerosi test sperimentali meccanici e termo-fisici hanno permesso di dimostrare che la nano-rete apporta miglioramenti rispetto al PVB standard solo sugli aspetti energetici mentre determina alcuni inconvenienti per quanto riguarda le problematiche meccaniche. Determina infatti:

- Maggiore assorbimento d'acqua, che potrebbe portare a fenomeni di delaminazione del vetro stratificato;
- Una riduzione dell'allungamento e del carico a rottura ma con un aumento della tenacità del materiale (tre parametri fondamentali che influenzano il comportamento globale del vetro stratificato);
- Una riduzione della capacità di adesione tra vetro e intercalare plastico con conseguente perdita di prestazioni della struttura;
- Leggera perdita di trasmittanza della luce visibile, ma significativo miglioramento nel range della radiazione solare.

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Chapter 1

Introduction

1.1 Background

The architectural and engineering trend leads towards greater use of glass in buildings. Growing safety awareness often requires laminated glass. Laminated glass is formed as a sandwich of two or more sheets of glass and a plastic interlayer, see Figure 1.1. Laminated glass can for example be used in stairs, floors, roofs, facades and balcony railings. The interlayer is typically soft polymers like polyvinyl butyral (PVB), ethyl vinyl acetate (EVA) and SentryGlas® (SGP) from the company DuPont. When laminated glass shatters, the plastic interlayer keeps the pieces of glass in place. This reduces the risk of cuts caused by splinters.

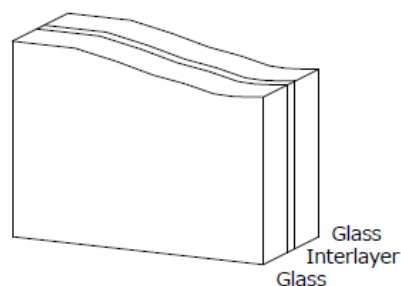


Figure 1.1 Laminated glass

Today there are many interlayers on the market with a large variation in their properties. For every project, in different areas of use, it is a challenging task to choose the most optimal interlayer.

PVB is the most common interlayer used in laminated glass and over years many new varieties of PVB have been developed. Previous works on the mechanical properties of the interlayer have mainly focused on standard PVB. More recent research has been done on SGP and the results have been compared to PVB. At this time, none or little research have been done comparing a new form of PVB.

1.2 Objective and Method

The main objective of this master thesis is to investigate a new form for PVB interlayers, shaping a nano-net, and compare their mechanical properties with traditional continuous layers. To evaluate the interlayers, both in standard form and in nano-net form, different tests were conducted (i.e., *Water Absorption Test*, *Tensile Test*, *Single-Lap Shear Test*, *Ageing Test*, *Scanning Electron Microscope and UV-Vis Test*).

The experimental tests and the numerical analyses led to draw guidelines on suitable interlayers for different field of applications.

1.3 Scope and Delimitation

The scope of the present thesis is to evaluate the mechanical properties of new PVB nano-net interlayers; moreover, comparison with other interlayer materials will be also conducted through existing research results.

1.4 Thesis Outline

The thesis is divided into several sections:

- Section 2 gives an introduction to the material glass and more detailed information about laminated glass.
- Section 3 explains the experimental test. The test specimens and procedures are also presented here.
- Section 4 presents a summary and a discussion of the results from the experimental tests.
- Section 5 discusses and draws conclusions from the results presented in section 4. Suggestions to possible further works are presented here.

Chapter 2

Laminated Glass

The mechanical properties of the interlayer and external glasses are of high importance when using laminated glass as a structural element.

In this chapter information of the material glass and laminated glass is provided. The first section treats the basics of glass, the manufacturing of float glass, the mechanical properties and post processing of float glass (heat-treated glass). In the second section laminated glass is described with information about the structural behavior, the post-breakage behavior, the properties of the interlayer and the current standards, guidelines and design methods for laminated glass.

2.1 Glass

Glass is a solid material that is hard and brittle. It is an amorphous solid, also called a non-crystalline solid, which means that the atomic structure is disordered [2]. Glass does not have an exact melting point like other materials; instead, it transforms from a liquid to a solid state over a certain temperature range, usually around 500°C. Glass unique characteristics are high transparency, resistance to corrosion and to many chemicals (which makes it a very durable material [2]), recyclability, as well as good mechanical properties and relatively low energy demand for its production.

There are numerous types of glass with varying chemical and physical properties depending on the area of use. The most common glass is the soda-lime glass, also called soda-lime-silica glass. Soda-lime glass contains the raw materials sand (contains silica), soda ash and limestone, and also a smaller number of various additives [2].

2.1.1 Manufacturing of Float Glass

Flat glass is the most commonly used glass in laminated glass and is typically made of soda-lime glass. Flat glass can be produced in different ways; however, the so-called float glass procedure stands for 90% of the production of flat soda-lime glass [3]. In the float process, invented by Pilkington in year 1959, the glass is produced by letting molten glass float on a bath of liquid tin, see Figure 2.1. By this procedure the glass gets a flat surface on both sides [2]. The thickness of float glass is controlled by the speed of which the glass is drawn off from the tin bath [4]. The glass is then cooled down slowly after the tin bath in the annealing lehr, which is a long tunnel oven [5, 3]. The annealing process removes the internal stresses in the material by the controlled cooling process. It is of high importance with controlled, slow cooling since uneven cooling can lead to a reduction of the mechanical strength. Another term for float glass is annealed glass. The last steps in the float process are inspection and cutting of the glass before delivering it to the customer [5]. However, the float glass can be processed further to produce glass products such as heat-treated glass and laminated glass, see Figure 2.2. The former is described in Section 2.1.3, while the latter is treated in Section 2.2.

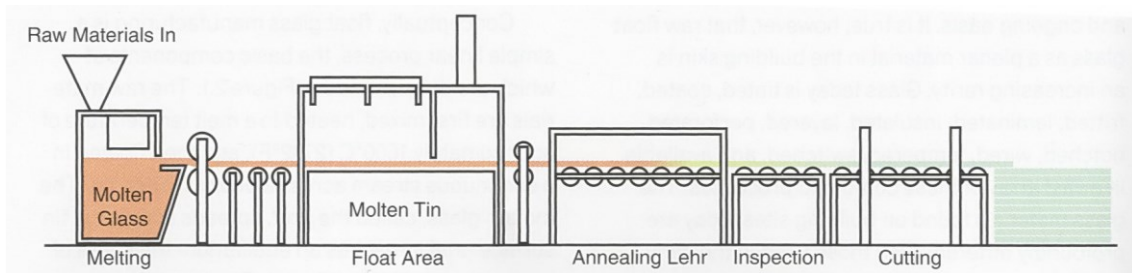


Figure 2.1 The float process

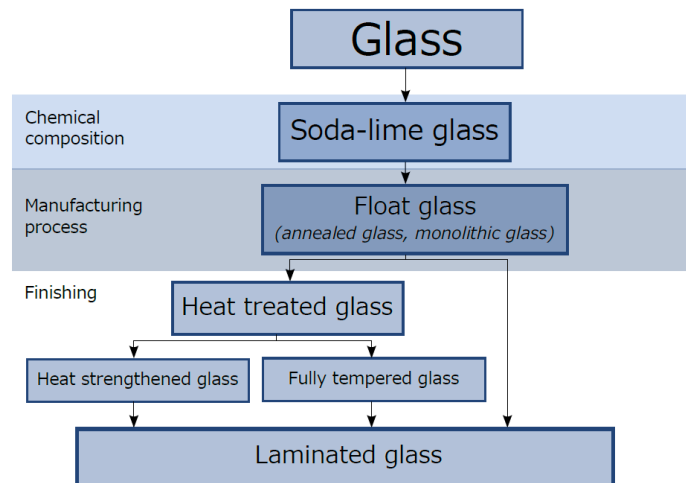


Figure 2.2 Overview of the most important glass products and the steps of processing

2.1.2 Mechanical Properties

Glass is an isotropic and a brittle material at normal room temperature with no inherent ductility [6, 7]. It deforms elastically under stress and shows no plastic deformation before fracture and it also cannot absorb energy in case of impact [6]. Consequently, the behavior of glass is deemed as ideally elastic [6]. The compressive strength is significantly higher than the tensile strength [3]. Glass is sensitive to micro-cracks and flaws for tension loading. Because of that, failure of glass generally occurs when tensile stresses are applied on small surface flaws that may appear during the manufacturing, transportation, assembly, or service life of glass.

The momentary strength for glass is time dependent. The strength decreases with time when the glass is subjected to a load and was discovered in 1899 by Grenet [6]. Glass is sensitive to stress concentration and high stress concentration is for example caused by surface flaws. Since glass shows no plastic behavior there is no stress redistribution to reduce the local stress concentration as in other material such as steel [6].

Flaws or defects play an important role regarding the mechanical strength. The practical value for the mechanical strength is always lower due to these defects [3]. The theoretical tensile strength, based on molecular forces, is very high, 32 GPa [6], while the practical value is much lower. Common values for the mechanical properties of glass are presented in Table 2.1.

Table 2.1 Mechanical properties of glass [2]

Compressive strength	880 – 930 MPa
Tensile strength	30 – 90 MPa
Flexural strength	30 – 100 MPa
Young’s modulus	70 – 75 GPa

2.1.3 Heat-treated Glass

As shown in Figure 2.2, laminated glass may be produced from annealed or heat-treated glass, also called tempered glass. The structural performance of laminated glass is dependent on the glass and the interlayer. The main advantage with heat-treated glass is its improved mechanical strength. Due to the higher strength, tempered glass is good option when enhanced load-bearing capacity is desired.

Annealed glass may be tempered in two ways; chemically or by a heat treatment. The chemically tempering is made by a process of ion exchange [6]. Chemical tempering is rare in structural applications, since this kind of tempering is only effective in very thin glass which are not common in buildings [5].

The mechanical strength of annealed glass may be further improved by a heat treatment, as done in the annealing step [5]. The heat treatment is often referred to tempering whereby the float glass is heated about 100°C above the glass transition temperature, approximately 600°C. in contradiction to annealing in the float process, the glass is then cooled down rapidly by jets of cold air, this is called quenching. The result of quenching is a glass with the surface in compression and the center in tension [6].

There are two kinds of heat-treated glass, the fully tempered glass and the heat strengthened glass. The fully tempered glass is made by the process described above. The latter, the heat strengthened glass, is produced in the same way, but with a lower cooling rate [6]. Fully tempered glass breaks into small harmless pieces so it is considered as a safety glass. Heat strengthened glass is not regarded as a safety glass since it breaks into larger pieces [5]. The fracture pattern depends on the energy stored in the glass. Due to the high residual stress release in fully tempered glass at the fracture (i.e., high energy) the material breaks into small fragments in contradiction to annealed glass that breaks into large shards [6]. One could say that heat strengthened glass is a material with properties between those of annealed glass and fully tempered glass. With a lower cooling rate, the mechanical strength is also lower for the heat strengthened glass. Fully tempered glass is four to five times stronger than annealed glass, whereas the heat

strengthened glass is two to three times stronger [5]. See Table 2.2 for a comparison of the heat-treated glasses.

Table 2.2 Comparison of heat-treated glass to annealed glass [5]

Type of glass	Fracture pattern	Mechanical strength
Fully tempered	Small, harmless pieces	4 – 5 times stronger
Heat strengthened	Larger pieces than fully tempered, but smaller than annealed glass	2 – 3 times stronger

Any work, such as cutting, drilling or grinding, on heat-treated glass needs to be done prior tempering. Another disadvantage with heat-treated glass is its risk for spontaneous breakage (i.e., the glass may shatter for no apparent reason). The cause for the spontaneous failure is nickel-sulphide inclusions in the glass, which is a small stone or a crystal [7, 5]. There is always a risk for nickel-sulphide inclusions during the production. The probability is very low, although not negligible due to the serious consequences of a spontaneous failure [6]. Annealed glass can also have nickel-sulphide inclusions but it is only a problem when it is present in heat-treated glass [5]. Due to the low cooling rate the nickel-sulphide particles are stable in annealed glass [2]. When annealed glass is subjected to a heat treatment, the nickel-sulphide particles increase in volume by the transformation into another state. This, in combination with the high tensile stresses in the glass core, is the cause for spontaneous breakage [6].

Spontaneous failure can occur days, or even years after production of heat-treated glass. To identify glasses containing nickel-sulphide additions, producers realize a so-called heat-soak test. By a heat-soak test the glass is slowly heated up and by maintaining a certain temperature, where the transformation of the particles occurs, the glasses that contain nickel-sulphide break [6]. The other glasses that do not break can be sold.

Heat-treated glass is more expensive due to the tempering process and the heat-soak test. Float glass exhibits very good optical properties and is largely free of distortion, but with a heat treatment visual distortion can occur. Therefore, heat-treated glass may have inferior optical properties [5]. Tempering leads to a reduction of the time-dependence of the strength [6]. The big advantage with tempered glass is, and may be pointed out twice, the high mechanical strength.

Values for the tensile strength in short-term tests for annealed, heat strengthened and fully tempered glass are presented in Table 2.3.

Table 2.3 Tensile strength in short-term tests [5]

Annealed glass	$\approx 30 - 90$ MPa
Heat strengthened glass	$\approx 50 - 120$ MPa
Fully tempered glass	$\approx 100 - 160$ MPa

2.2 Laminated Glass

Laminated glass was invented in year 1909 by the French chemist Eduard Benedictus [8]. Laminated glass is used in many different fields of applications, such as in buildings, but also in airplane windows and windscreens in cars.

Laminated glass was in the beginning developed as a product with better load-bearing capacity than monolithic glass [5]. But laminated glass also has other desirable properties such as enhanced safety, security, fire resistance and sound attenuation properties [5, 6]. The resistance on impacts, such as bullets, and the resistance to blast loads is higher for laminated glass due to the plastic interlayer [5, 6]. By laminating the post-breakage behavior is enhanced, therefore laminated glass is useful in structural applications [6].

Laminated glass consists, as mentioned before, of two or more sheets of glass bonded together by a plastic interlayer [2]. Laminated glass that consists of more than two sheets of glass are called a multiply and these are for example used in glass beams, columns, stair treads and landings [5]. The adhesive contact between the glass and the interlayer is made by high pressure and heat, around 140°C. this process generally takes place in a vessel, the autoclave [2, 5].

The purpose of the interlayer is to retain the fragments after fracture in the laminated glass, which eliminate the risk of injury due to glass shards [5, 6]. Laminated glass may consist of different kinds of glass and interlayers, see Figure 2.3. The thickness of the panes may be equal or unequal and the panes can be annealed glass, heat-treated glass or a combination of the two [5, 6].

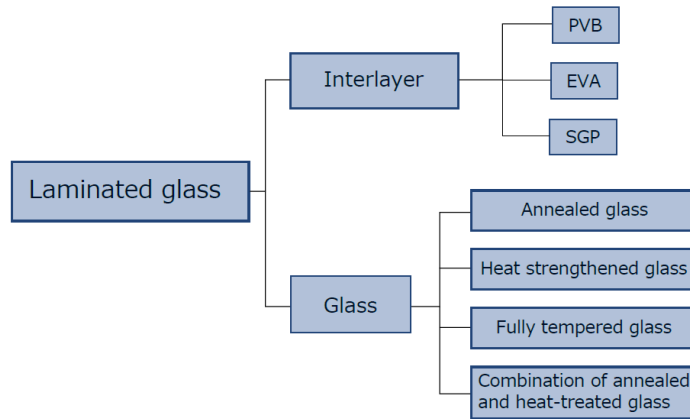


Figure 2.3 Components of laminated glass

The interlayer used in laminated glass is for example polyvinyl butyral (PVB), ethyl vinyl acetate (EVA) and SentryGlas® Plus (SGP) from the company DuPont, see Figure 2.3. Laminated glass can also consist of a liquid resin instead of a sheet interlayer. This is not so common and will not be treated in this thesis [5].

2.2.1 Interlayers

There is a variety of interlayers on the market, which are suitable for different areas of use. Interlayers can be used as a decorative effect with tinted or patterned interlayers, which will give the building a different aesthetic look. Some interlayers are addressed to improve the thermal or acoustic performance, the fire resistance and the safety and security properties.

The interlayers in laminated glass works in a wide range of temperatures, since it is usually subjected to different temperatures due to the seasonally changing weather (winter, summer). The interlayers are also subjected to loads with different time spans, such as impacts and permanent loads. Consequently, it is important to evaluate the mechanical properties at different temperatures and times.

Interlayers used in laminated glass units are polymers with viscoelastic behavior [9]. Materials with viscoelastic properties are dependent on time, temperature and load. These parameters influence the properties in different ways, for example: the higher the temperature, the weaker the interlayer. The interlayers creeps with high loads and with long loading time. Therefore, it is common to assume that the interlayer creeps for sustained loads (i.e., ignore any shear transfer between the glass panels). By short load durations one may assume some shear interaction [6]. PVB, the most common interlayer, can usually transfer full shear stress between the two sheets of glass at a temperature below 0°C and for shorter times of loading.

The ability to transfer shear stress is reduced by higher temperature and longer times of loading. Interlayers in laminated glass are usually soft polymers like SGP, EVA or PVB.

PVB (polyvinyl butyral) was the first material used as interlayer for laminated glass in the thirties. It is formed from the reaction of polyvinyl alcohol with butyraldehyde. PVB can be defined as an amorphous random terpolymer and it is composed of three different monomers, see Figure 2.4, providing specific properties [10]:

- Vinyl butyral (76 – 80 wt%) (x): this unit is hydrophobic, elastic and provides good processability and compatibility with many plasticizers.
- Vinyl alcohol (18 – 22 wt%) (y) and vinyl acetate (1 – 2 wt%) (z): these units provide high adhesion to inorganic materials such as glass and are hydrophilic.

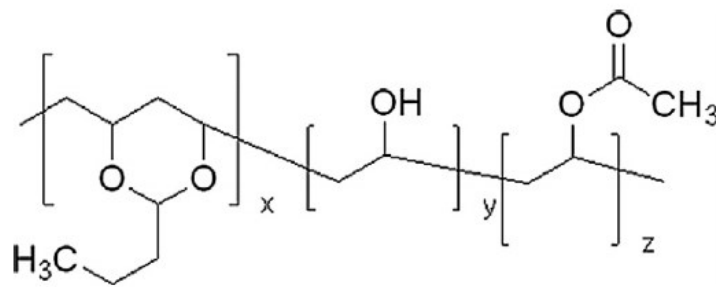


Figure 2.4 PVB chain structure [10]

PVB chains with higher molecular weight provide toughness to the interlayer; therefore, plasticizers must be incorporated in order to improve the material elasticity. The synthesis process can be divided in three main steps. The first one is the polymerization of vinylacetate in a chain of poly(vinylacetate). Afterwards, this chain is hydrolyzed which leads to the formation of poly(vinylalcohol). In the last step it reacts with butyraldehyde to form butyl cyclic compounds [10]. This polymer provides excellent optical and mechanical properties to laminated glass (see Table 2.4), high mechanical strength, high deformation before breakage, good adhesion to glass (after lamination process), and high light transmission [10]. On the other hand, it is important to point out that weathering conditions may degrade PVB: ambient humidity may cause a loss in the adhesion with glass and ultraviolet radiation may decrease its mechanical properties [10]. New types of PVB have been more recently developed in order to improve some of its properties for certain

applications. For example, structural PVB is based on PVB but with a lower level of plasticizer, which increases its glass transition temperature and therefore its stiffness. There is also the possibility to improve other properties of the PVB, for example, increase its transparency or its acoustic insulation [10].

Table 2.4 Commercial PVB main properties (foil thickness 0.76 mm) [10]

Parameter	Value	Units
Standard PVB		
Price	4.02 – 4.82	€/m ²
Density	915 – 1070	kg/m ³
Water absorption	3.6	wt. %
Coefficient of thermal expansion	22 – 40	K ⁻¹ · 10 ⁻¹⁵
Transmittance	88 – 89	%
Yellowness index	12.5	-
Ultimate tensile strength	20.8	MPa
Elongation at failure	190 – 350	%
Young modulus	n.a.	MPa
Poisson's ratio	0.5	-
Glass transition temperature	8 – 42	°C
Joining technique	Lamination, UV curing	-
Structural PVB		
Ultimate tensile strength	33	MPa
Elongation at failure	190	%
Young modulus	2.36	MPa

In 1964 the term “*ionomer*” (*SGP*) was registered by DuPont® for the first time. Ionomers are a type of ionic polymers which have an ionic content of at most 10 mol% within a non-polar polymer [10]. In general terms, the structure of an ionomer consists of a hydrocarbon backbone containing pendant acid groups which are partially or completely neutralized. The synthesis of ionomers is achieved through copolymerization of functionalized monomers. Ionomers typically achieve high levels of stiffness throughout crosslinking. In this case crosslinking is not obtained through the addition of Sulphur (vulcanization) but with metal ions which act as physical crosslinking points [10]. Therefore, this material can be classified in the group of thermoplastics, see Figure 2.5.

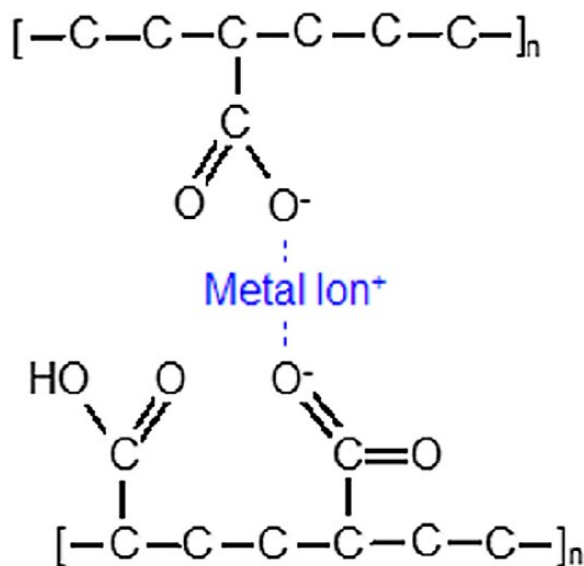


Figure 2.5 Chemical structure: metal cation bridges two carboxylate anions [10]

SentryGlas, developed by DuPont®, presents high stiffness over a wide temperature range and high transparency. Since it is a viscoelastic material, its stiffness depends on the load duration and the working temperature, but it is much stiffer and less sensitive to load duration and working temperature than other interlayers such as PVB [10]. For some mechanical properties of SGP, see Table 2.5.

Table 2.5 Commercial SentryGlas main properties (foil thickness 0.76 mm). Values come from technical data sheet provided by the manufacturer [10]

Parameter	Value	Units
Price	n.a.	€/m ²
Density	950	kg/m ³
Water absorption	n.a.	wt.%
Coefficient of thermal expansion	10 – 15	K ⁻¹ · 10 ⁻¹⁵
Transmittance	n.a.	%
Yellowness index	2.5	-
Ultimate tensile strength	34.5	MPa
Elongation at failure	400	%
Young modulus	300 – 480	MPa
Poisson's ratio	0.442 – 0.500	-
Glass transition temperature	55	°C
Joining technique	Lamination	-

EVA (Ethylene-vinyl acetate) is the copolymer of ethylene and vinyl acetate (VA), see Figure 2.6, in which the weight percentage of vinyl acetate varies from 10 wt% to 40 wt%, thus belonging to polyolefins. By varying the VA content in the composition, EVA with significantly different properties is obtained [10].

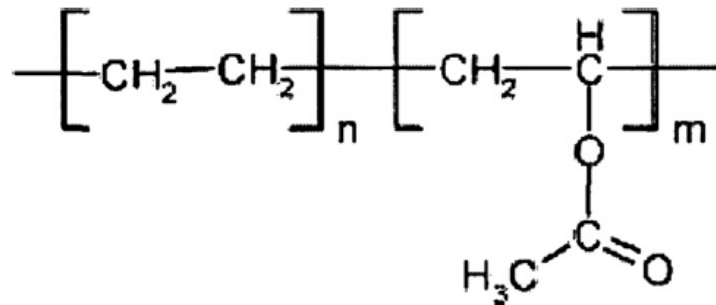


Figure 2.6 EVA contains ethylene groups (n) and vinyl acetate groups (m) [10]

As an interlayer material EVA provides stress-crack resistance, high flexibility, toughness, elasticity and clarity. As shown in Table 2.6, EVA also provides certain unique properties such as high electrical resistivity, excellent optical transmission, low fusion and polymerization temperature, and resistance to weather conditions: both solar radiation and moisture (waterproof resistance). EVA is cured in a vacuum lamination oven at 140 – 155 °C. vinyl acetate units are chemically attached to each other during this curing process, crosslinking into a three-dimensional structure. Fundamental properties such as creep rupture, tearing resistance and chemical resistance can be greatly increased due to the crosslinking [10].

Table 2.6 EVA interlayer main properties (foil thickness 0.76 mm) [10]

Parameter	Value	Units
Price	1.74 – 1.91	€/m ²
Density	945 – 955	kg/m ³
Water absorption	0.15 – 0.50	wt.%
Coefficient of thermal expansion	160 – 190	K ⁻¹ · 10 ⁻¹⁵
Transmittance	90 – 92	%
Yellowness index	1.9	-

Ultimate tensile strength	9.5 – 10	MPa
Elongation at failure	880 – 930	%
Young modulus	7 – 9	MPa
Poisson's ratio	0.47 – 0.49	-
Glass transition temperature	-77 to -69	°C
Joining technique	Vacuum lamination	-

Polyurethane (PU) materials are a wide variety of polymers where all polymer composed of organic units joined by urethane links are included. Interlayer polyurethane are composed of *thermoplastic polyurethane (TPU)*, also known as polyurethane elastomer. These polymers are block copolymers with rubbery soft segments and semicrystalline or glassy hard segments. In the one hand, soft segments available are of great extension and will determine properties of the material and its application. On the other hand, hard segments consist of diisocyanatos and short chain diols [10].

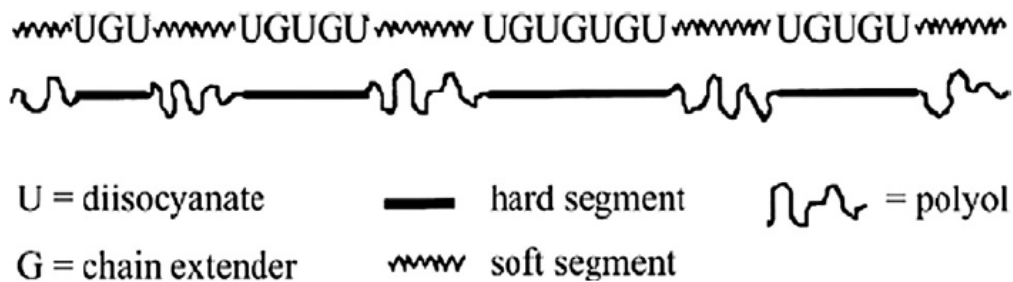


Figure 2.7 Hard and soft segments of TPU structure [10]

As an interlayer material, TPU provides a combination of outstanding properties: high tensile strength, toughness, resistance to UV, abrasion and chemical degradation. In can be laminated at lower pressures and with different material combinations. On that account, TPU is often used in hybrid components for security and ballistic resistant glass applications. Nowadays, TPU is not widely used due to its high price. In addition, as a recently developed material, TPU interlayers have not as much certifications as PVB and studies are still being carried out [10].

2.2.2 Structural Behavior of Laminated Glass

The structural behavior of laminated glass is complicated. There have been many researches conducted within this field, mostly research deals with beams and plates of regular geometries subjected to standard point loads or uniformly distributed loads [11].

One of the first studies on the structural behavior was carried out by J.A. Hooper who conducted a research on laminated beams subjected to four-point bending [12]. The outcomes were then used for the structural design of the glass walls for Sydney Opera House [12]. The conclusion from the work was that the bending strength is dependent on thickness and modulus of the interlayer. The study also demonstrated that when laminated glass is subjected to sustained loads, such as snow or self-weight load, the laminated glass unit should be considered as two independent glass layers [12].

Two models to describe the structural behavior are often mentioned in previous works, the layered glass unit model mentioned by Hooper and a monolithic glass plate model. A monolithic glass plate model is a simple model that consists of a monolithic glass, while the layered glass unit model consists of two sheets of glass and no interlayer, see Figure 2.7. The behavior of laminated glass units is somewhere between these two models. The real behavior may be calculated by the finite element method. An article dealing with this matter was conducted by Behr, Minor, Linden and Vallabhan in year 1985 [13]. The main objective of the study was to determine whether the structural behavior of laminated glass units is best characterized by the monolithic or the layered behavior. The study was conducted on plates, instead of beams as in the work conducted by Hooper. The conclusion from the study was that the laminated glass behaved like a monolithic glass plate with equal glass thickness in room temperature. However, at elevated temperatures it deflects like a layered glass unit having the same thickness [13].

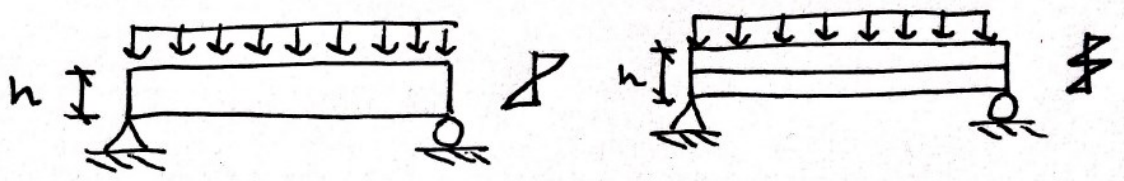


Figure 2.8 Stress distribution along cross section; monolithic and layered unit

2.2.3 Post-breakage Behavior

Laminated glass has enhanced post-breakage behavior compared to monolithic glass panes. The behavior can be described in three stages, see Figure 2.8, where both glass sheets are intact in the first stage. In the next stage, stage two, the bottom glass panel is fractured and the top panel is carrying all the loads. In the stage three the top sheet is also fractured; the interlayer is in tension and the glass pieces are locked together in compression [6].

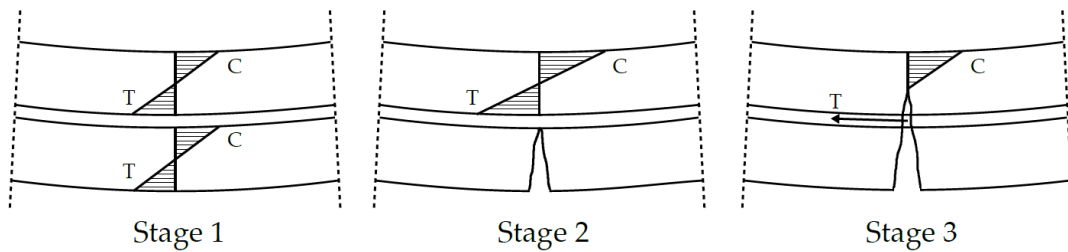


Figure 2.9 Post-breakage stress distribution, T = tension, C = compression

There is a risk for so called dropouts in stage three, for example when laminated glass is used in ceiling or roofs. Dropouts may happen when both glass plies have broken and the interlayer is carrying the load. The glass panel may then separate from the support and fall down [5]. The risk of dropouts is higher for laminated glass units made of fully tempered glass. It is good to avoid fully tempered glass in laminated glass due to the post-breakage behavior. However, it may be used in combination with annealed or heat strengthened glass. If the laminate consists of one fully tempered glass, it is important that the fully tempered glass pane is located on the tensioned side of the laminated unit [6].

The remaining load-bearing capacity after failure is dependent on the fragmentation of the glass, and as a consequence on the type of tempering process, and type of interlayer. Larger fragments lead to better post-break behavior of the laminated glass. Due to the fracture pattern with very small pieces, the post-failure performance by fully tempered glass is less favorable than that of annealed glass. The fully tempered glass will sag like a wet towel and the post-breakage capacity relies solely on the tensile strength of the interlayer in this case. Therefore, the stiffness and the tensile strength of the interlayer are very important properties for the post-breakage structural capacity. Accordingly, it is important to choose the right type of glass and interlayer for the application when designing laminated glass

as a structural element, since the remaining load bearing capacity is dependent on these [6].

2.3 Current Standards, Guidelines and Design Methods

The current standards and guidelines for glass is not sufficient since they do not apply to all type of glass configurations, loading and support conditions [6]. Most of the guidelines only cover glass element of rectangular shape with continuous support and to uniformly distributed out-of-plane loads [6]. In the other words, there are no simple guidelines for designing a structural element made of glass. One design method is to carry out experimental tests. However, it is expensive and not reliable as long-term design method.

In the draft for the European standard (prEN 16612: Glass in building – Determination of the load resistance of glass panes by calculation and testing) the engineer is advised to do finite element simulations or to use a simplified calculation method to determine the load resistance of laminated glass. It also states that the viscoelastic properties of the interlayer material shall be considered when calculating the resistance to bending of laminated glass. One shall also take into account the variation with temperature and load duration for the interlayer. The viscoelastic properties of the interlayer shall be determined according to prEN 16613. In this standard one shall undertake tensile test to determine the shear modulus. It also prescribes that one shall do other tests regarding the time dependent behavior.

Chapter 3

Experimental tests

Experimental tests were performed at the laboratory of “Dipartimento di Ingegneria Civile, Edile ed Architettura” and at the laboratory of “Dipartimento di Scienze e Ingegneria della Materia, dell’Ambiente ed Urbanistica” at Università Politecnica delle Marche. The purpose of the experimental tests was to determine the mechanical, physical and optical properties of PVB interlayers in two different forms, foils (as in traditional applications) and nano-nets. This was done with several tests as shown in this chapter.

3.1 Specimens Design

All the PVB specimens used for this thesis were obtained from a large PVB sheet (Saflex® Clear PVB interlayer) produced by Eastman and supplied by Nova Vetro S.r.l.

The collaboration between Università Politecnica delle Marche and Nova Vetro S.r.l stems from the need to develop and test a new type of PVB that has performance comparable to SentryGlas® but with a lower cost than the latter (SentryGlas® has a price equal to 40% more than traditional PVB). The aim of manufacturer Nova Vetro is to use innovative materials, within its production chain, which lead to an increase in the value of the company and the products supplied.

This industrial vision, combined with the academic experience in new components development and a broad background of PVB studies, led to the realization of this thesis.

3.1.1 Standard PVB Interlayer Specimens

The standard PVB sheets come in the form of a whitish opaque film rough to the touch. Its stiffness varies according to the room temperature in which it is found: at a temperature above 20 °C the PVB film begins to completely lose its stiffness and opacity, passing to a soft and transparent consistency; the loss of stiffness is associated also to a reduction of the main mechanical properties. For this reason, the PVB is kept inside thermal blankets, characterized by a low emissivity value to minimize heat exchange, in controlled climatic chambers with temperatures below 12 ° C and relative humidity below 50%. Figure 3.1 and Figure 3.2 show what PVB looks like in different conditions of temperature and humidity.

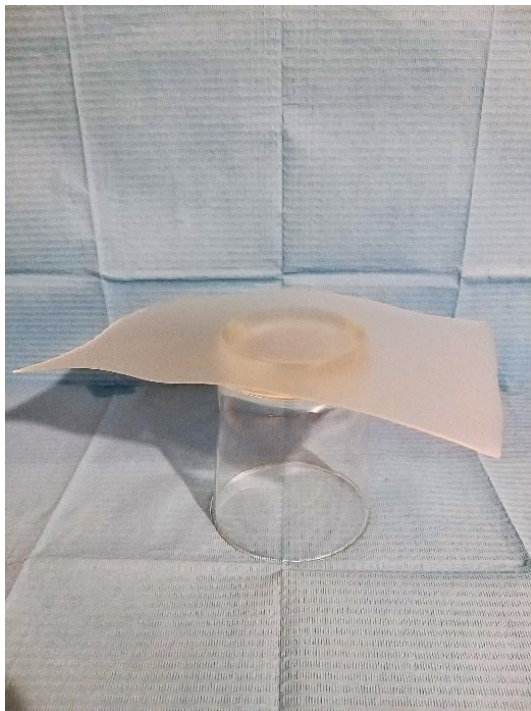


Figure 3.1 PVB specimen at 7 °C and 50% RH

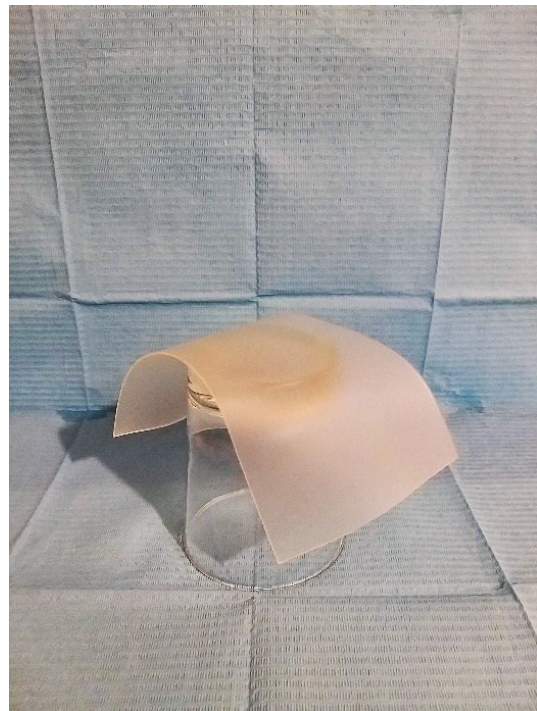


Figure 3.0.2 PVB specimen at 20 °C and 65% RH

SEM – Scanning Electron Microscope

Morphological observations of standard PVB (one 0.76 mm thick sample) were performed using Scanning Electron Microscopy (SEM) by TESCAN ANALYTICS™ VEGA3 operating at 10.0 kV. The sample was gold plated before putting for the SEM analysis. Micrographs were recorded at 5, 50 and 100 μm. The overall thickness parameter of standard PVB film was deduced from the product data sheet.

SEM analysis showing surface morphology of standard PVB are presented in Figure 3.3, Figure 3.4 and Figure 3.5. As shown in the following figures, standard PVB is characterized by a homogeneous and flat surface without particular evidences at the nanometer scale.

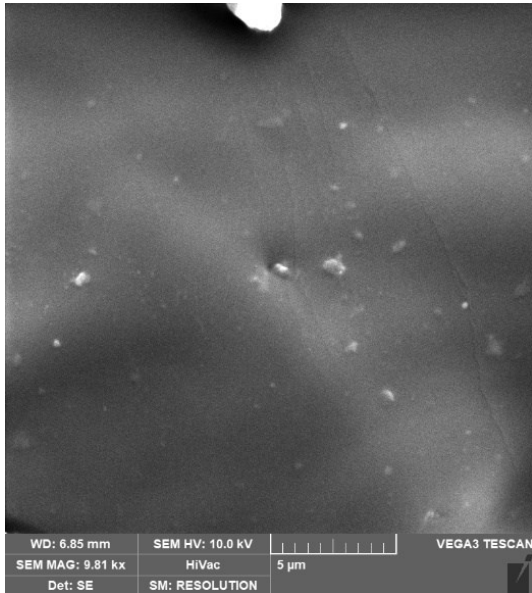


Figure 3.3 SEM image at 5 μm - Standard PVB

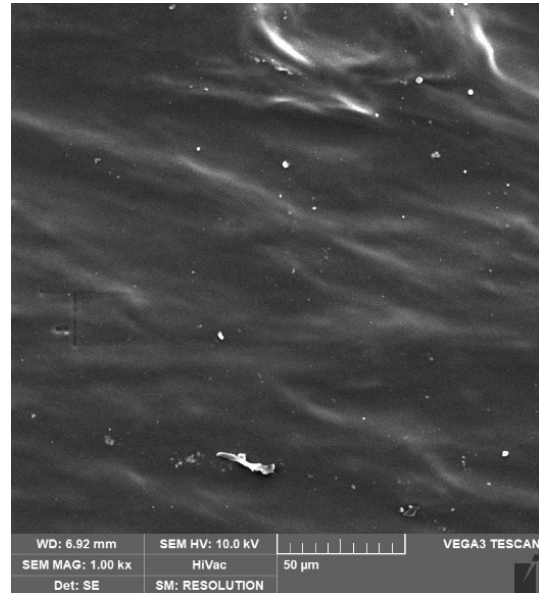


Figure 3.4 SEM image at 50 μm - Standard PVB

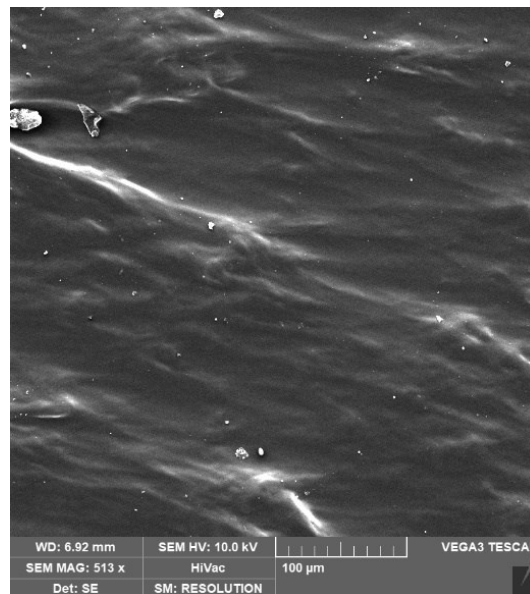


Figure 3.5 SEM image at 100 μm - Standard PVB

3.1.2 Nano-net PVB Interlayer Specimens

Electrospinning

Electrospinning is a fiber production method which uses electric force to draw charged threads of polymer solutions or polymer melts up to fiber diameters in the order of some hundred nanometers. The process does not require the use of coagulation chemistry or high temperatures to produce solid threads from solution. This makes the process particularly suited to the production of fibers using large and complex molecules [26].

When a sufficiently high voltage is applied to a liquid droplet, the body of the liquid becomes charged, and electrostatic repulsion counteracts the surface tension and the droplet is stretched; at a critical point a stream of liquid erupts from the surface. This point of eruption is known as the Taylor cone. As the jet dries in flight, the mode of current flow changes from ohmic to convective as the charge migrates to the surface of the fiber (Figure 3.6). The jet is then elongated by a whipping process caused by electrostatic repulsion initiated at small bends in the fiber, until it is finally deposited on the grounded collector (Figure 3.7). The elongation and thinning of the fiber resulting from this bending instability leads to the formation of uniform fibers with nanometer-scale diameters [26].

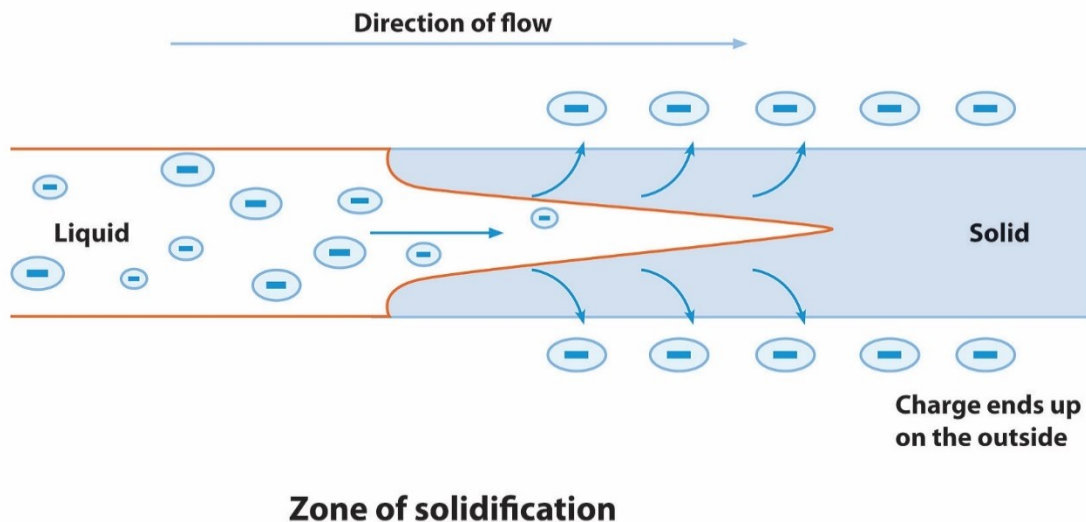


Figure 3.6 How the distribution of charge in the fiber changes as the fiber dries during flight [26]

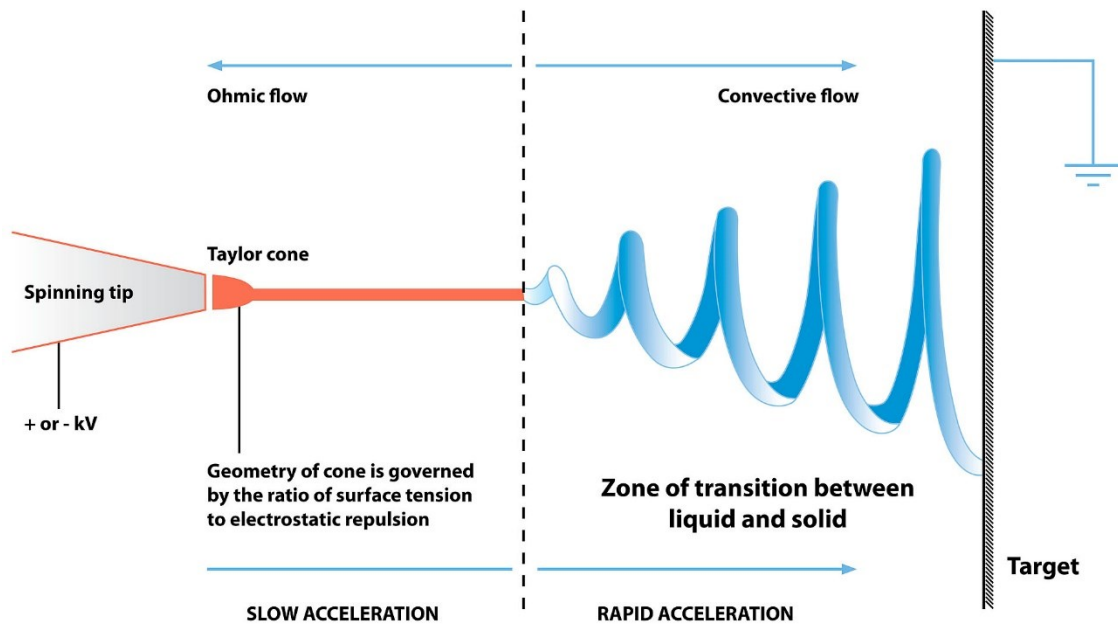


Figure 3.7 Diagram showing fiber formation by electrospinning [26]

The standard laboratory setup for electrospinning consists of a spinneret (typically a hypodermic syringe needle) connected to a high-voltage (5 to 50 kV) direct current power supply, a syringe pump, and a grounded collector (Figure 3.8). A polymer solution, sol-gel, particulate suspension or melt is loaded into the syringe and this liquid is extruded from the needle tip at a constant rate by a syringe pump. Alternatively, the droplet at the tip of the spinneret can be replenished by feeding from a header tank providing a constant feed pressure. This constant pressure type feed works better for lower viscosity feedstocks [26].

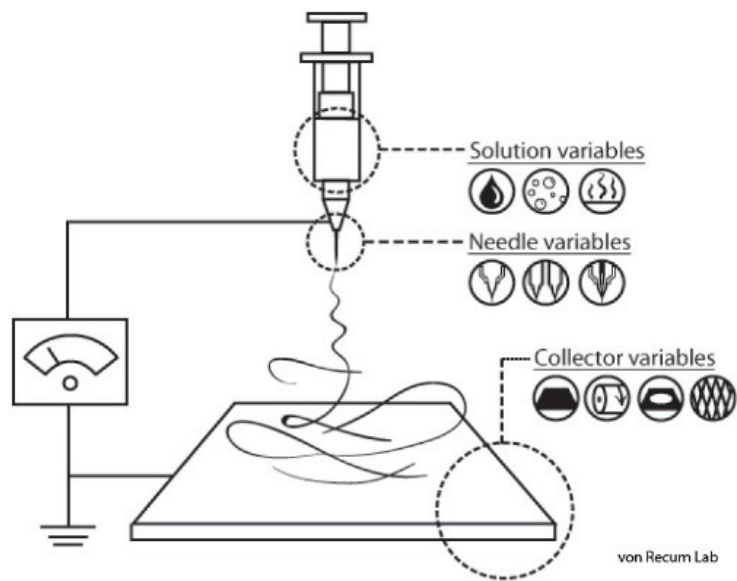


Figure 3.8 Electrospinning/electrospraying schematic with variations for different processing outcomes [26]

Materials and methods

Fabrication of electrospun nano-net fibers was performed using a semi-automatic electrospinning machine (Spinbox by Bionicia®) which is composed by (Figure 3.9):

- Syringe feeding system (A);
- Electrospinning box with a syringe needle (B) connected to a high voltage current power supply and a flat collector (C).

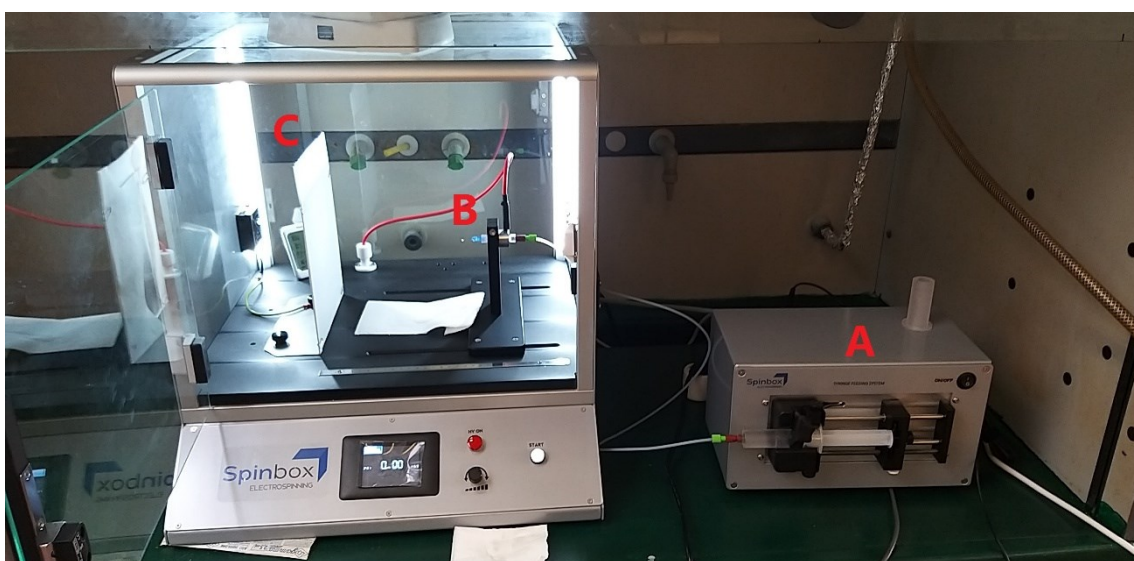


Figure 3.9 Setup for electrospinning (Spinbox by Bionicia®)

After accurately measuring the water content in standard PVB through Tg (0.7%), polymeric solution was prepared by dissolving Polyvinyl Butyral (12%, Saflex® Clear PVB, Eastman) in Ethanol (EtOH, 88%) for more than 24 h. The solution was then stirred by a magnetic stirrer for a few minutes in the ambient temperature to reach preferable polymer-solvent interactions.

To start the production process, the syringe and the tube, that connects the syringe to the needle, were filled with the solution without leaving air bubbles inside. The flat collector was covered with parchment paper as it allows to easily peel off the nano-net PVB specimen. The electrospinning parameters were set at:

- Voltage = 23 kV;
- Collector distance = 22 cm;
- Syringe diameter = 20.05 mL;
- Pumping rate = 7.00 μ L/min
- Target volume = 18.00 mL

For the entire duration of the process, a temperature of 25 °C and a relative humidity of less than 40% was maintained through the use of a dehumidifier and an electric heater.

All collected specimens were placed and kept in a desiccator with moisture absorbing salts to prevent moisture from trapping in the cavities within the nano-net.

SEM – Scanning Electron Microscope

Morphological observations of as-synthesized PVB nano-net (three samples with different thickness) were performed using Scanning Electron Microscopy (SEM) by PHILIPS™ XL20 operating at 15.0 kV. Briefly, as-prepared samples were dried in desiccator for 24 hours and gold plated before putting for the SEM analysis. Micrographs were recorded at 10 μ m and nanofibers thickness at the surface was measured using ImageJ software. The overall thickness parameters of each PVB nanoweb film was calculated by mounting each sample with the glass (microscope slide) and scrolling towards the lens at 90° under Olympus™ BX51 microscope.

SEM analysis showing surface morphology and thickness parameters of PVB nano-net are presented in Figure 3.10. Nanoweb for each sample is forming homogenous network with overall thickness in the range between 800 – 1300 nm. However, due to variation in the volume of PVB electrospun solution, the thickness parameters of each sample were different. PVB electrospun solution having the volume of 6

mL, 12 mL and 18 mL, give rise to the thickness of 192-201 μm , 236-251 μm and 311-328 μm , respectively.

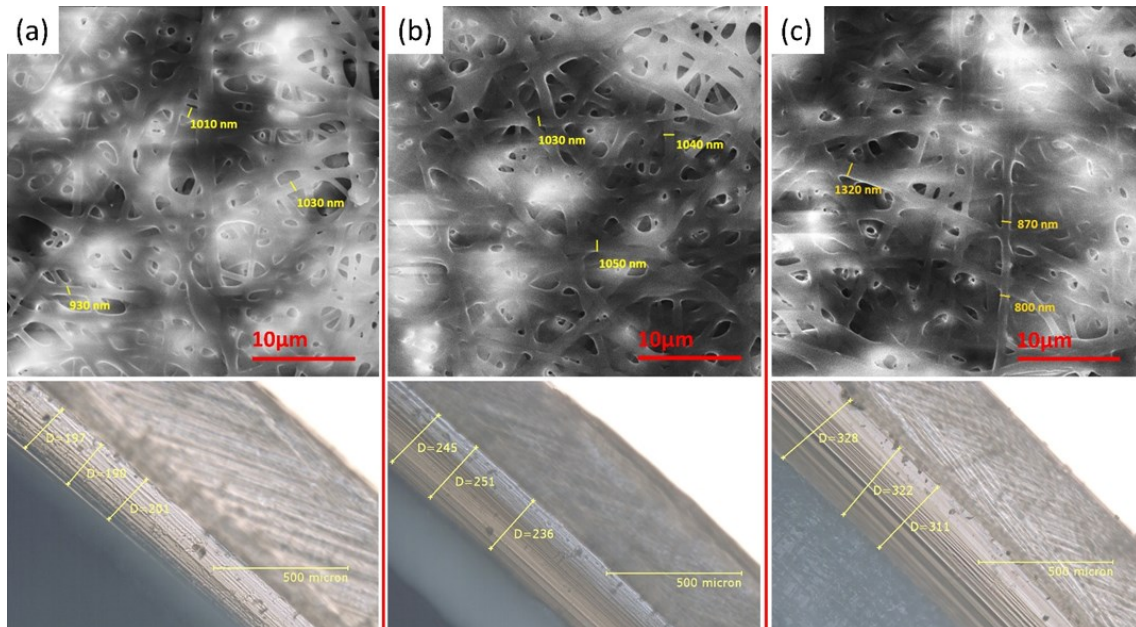


Figure 3.10 Surface morphology and thickness parameters of nano-net PVB

3.2 Water Absorption Test

Water Absorption Test was carried out according to the UNI EN ISO 62:2008 [17].

Three (3) square-shaped specimens 60 x 60 mm (dimensions given in ISO 294-3) were chosen for this test. They were obtained by cutting them from a larger PVB sheet with a cutter. Then, any contaminant on the test specimen surface, which could influence water absorption, were removed by a cleaning agent which does not attack the plastic. Clean gloves were worn when handling the test specimens to prevent contamination. Figure 3.11 shows PVB specimen used to perform this test.

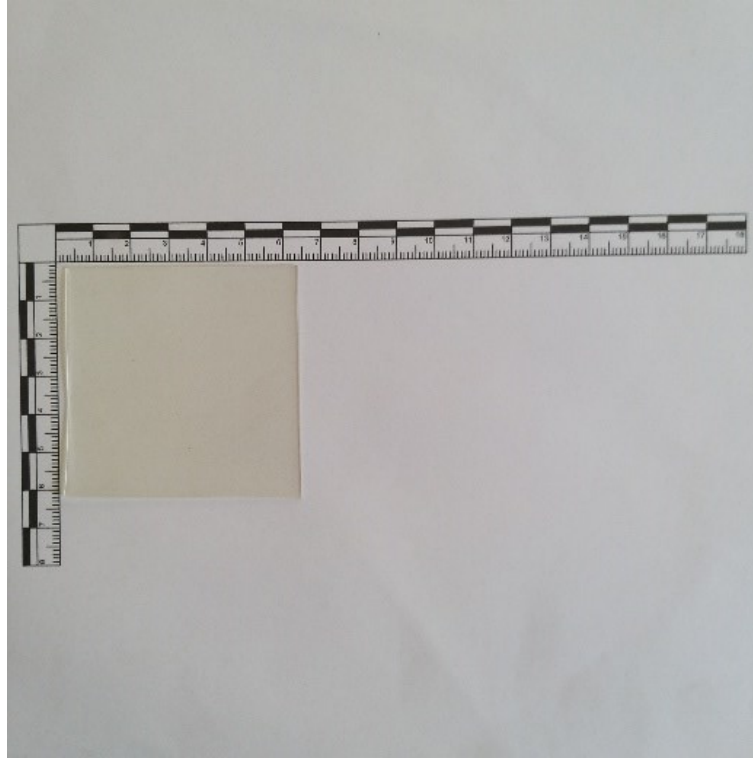


Figure 3.11 PVB specimen for water absorption test

The main idea of the water immersion test was to simulate a long-term exposure to a humid weather in buildings. Three square samples were cut into 60 x 60 mm and oven dried at 50 °C (± 1 °C) for 24 h and then allowed them to cool at room temperature in the desiccator (mass m_1). Next, each test specimens were laced in a container filled with distilled water (8 ml per square centimeter, 300 ml per test specimen) and maintained at 23.0 °C \pm 1,0 °C (see Figure 3.12). After the immersion for 24 h \pm 1 h, the specimens were removed from the water, surface was cleaned with a dry cloth and weighted using analytical and precision balance (Kern-770™) within 1 min of removing them from the water ($m_{2/24 h}$). The water content at saturation was measured by re-immersing the test specimens and reweighted at given time intervals. A typical immersion time scale was 24 h, 48 h, 72 h, 96 h, 120 h, 144 h, 168 h, 192 h, and 216 h. At each of these intervals, test specimens were removed from the water, cleaned all surface water, and each test specimen was reweighted within 1 min of removal from water (e.g., $m_{2/24 h}$). The mass increase is associated to the water absorption.

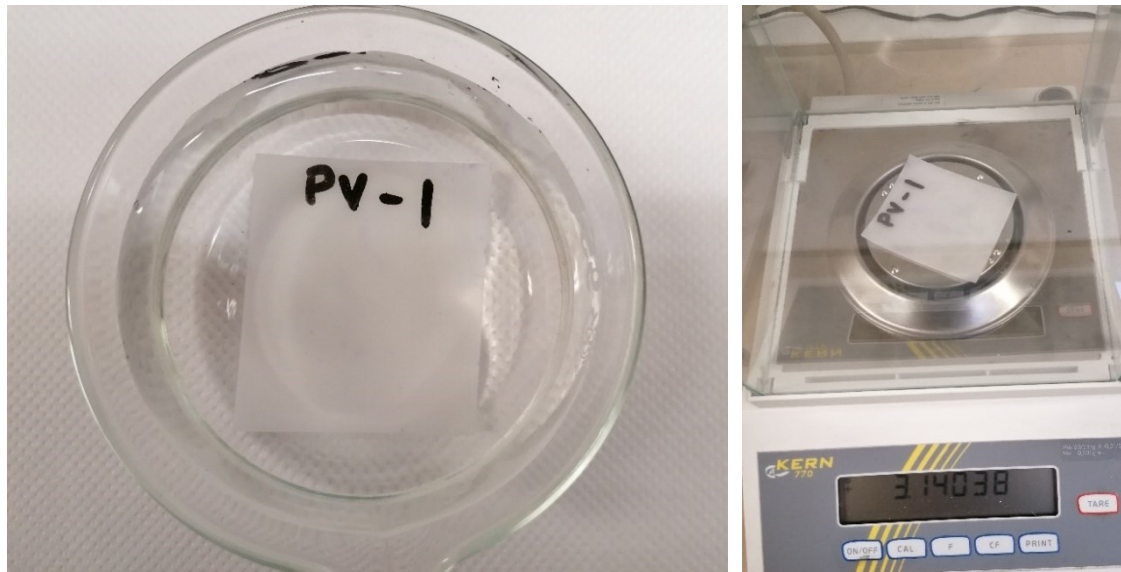


Figure 3.12 Setup for water absorption test

3.3 Tensile Test

Tensile test was done according to UNI EN ISO 527-3 [19].

The test specimen form for the determination of tensile properties by that method was a strip that was 25 mm wide and 190 mm long, having two parallel gauge marks, 50 mm apart, on the central portion of the specimen. Five (5) specimens were obtained by cutting them from a larger PVB sheet with cutter capable of cutting the specimens to the proper width and producing straight, clean, parallel edges with no visible imperfections.

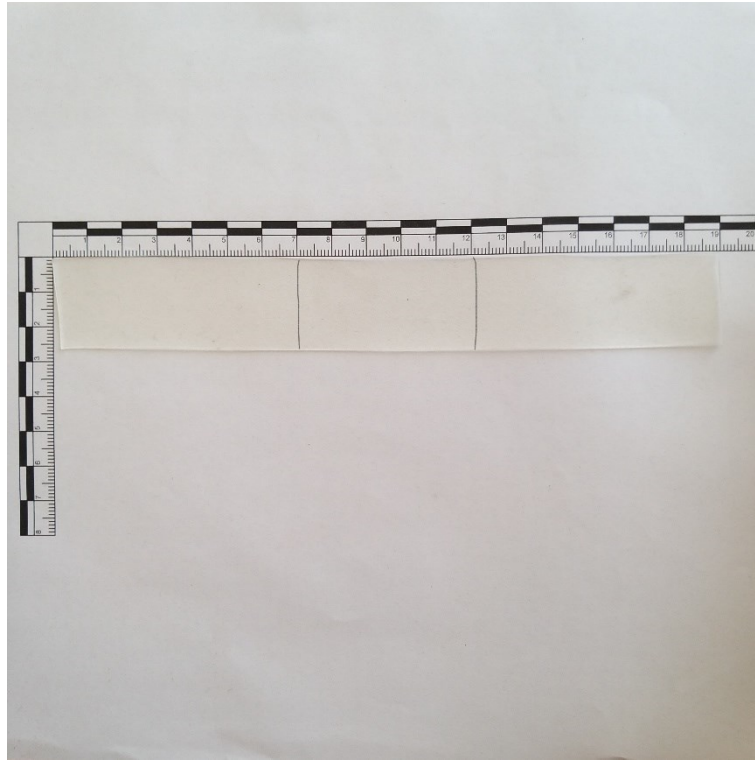


Figure 3.13 PVB specimen for tensile test

The uniaxial tensile tests were performed at room temperature. Each specimen was placed in the grips, taking care to align the longitudinal axis of the test specimen with the axis of the testing machine (Zwisch Roell Z050 with a 5'000 N load cell). The grips were tightened evenly and firmly to prevent slippage of the test specimen and movement of the grips during the test. Care was taken to ensure that gripping pressure did not cause fracture or squashing of the test specimen.

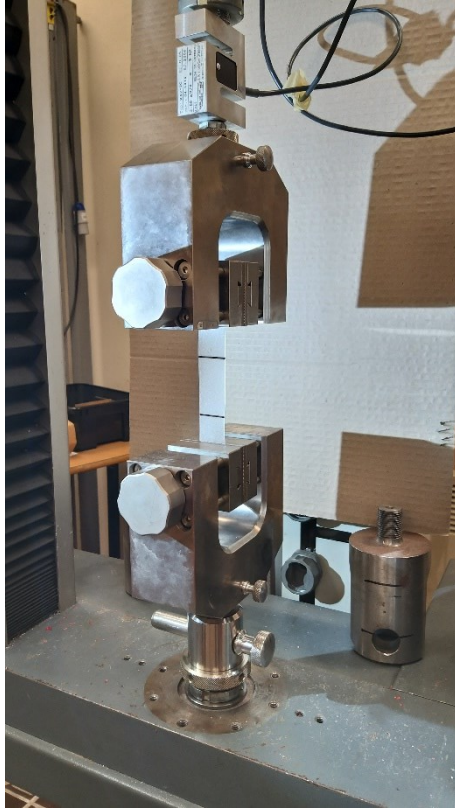


Figure 3.14 PVB specimen placed in the grips of Zwick Roell Z050

After placing the test specimen, a camera (Pixelink PL-B) for optical elongation measurement was set up and adjusted. An elongation rate of 10 mm/min was set (in this thesis the time dependence of the PVB mechanical properties is not studied). The rupture was almost always located close to one of the clamps due to the high stress concentration there.

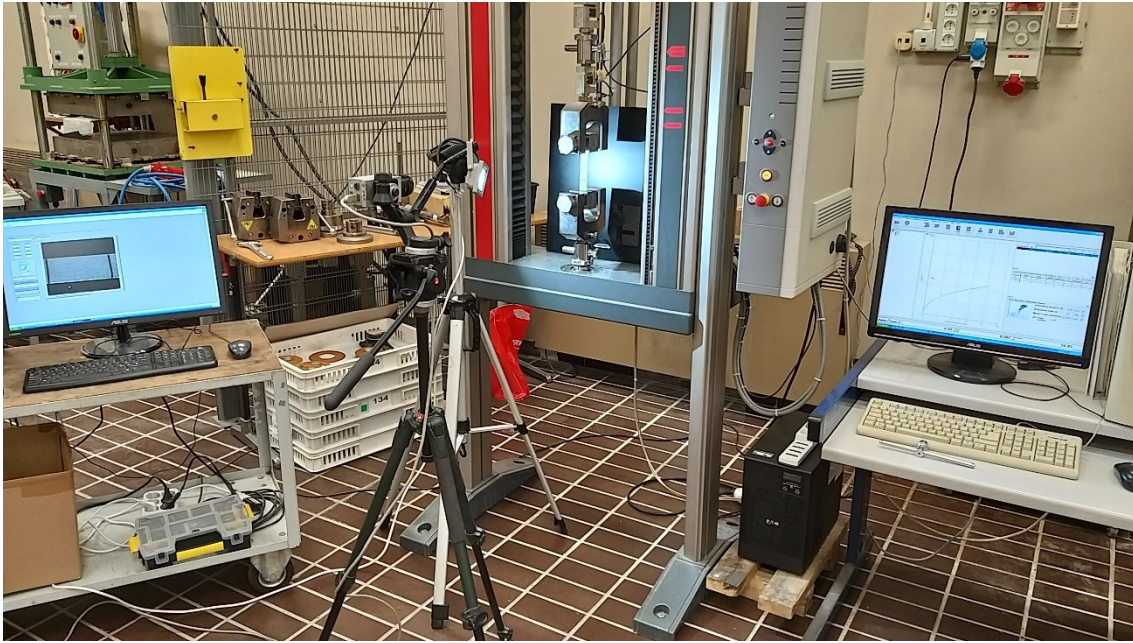


Figure 3.15 Setup for tensile test

3.4 Single Lap-Shear Test

Single lap-shear test was done according to UNI EN 1465:2009 [20].

The test specimens for this test were obtained by bounding two 8 mm monolithic pieces of clear glass 100 mm long and 180 mm wide, with 20 mm of overlap filled with PVB. The composition of the laminated glass was: 8 mm clear glass + PVB + 8 mm clear glass. The sandwiches were obtained with a lamination process carried out in Nova Vetro S.r.l in an autoclave for 4 hours at a fixed temperature of 128 °C and a pressure of 7 bar.

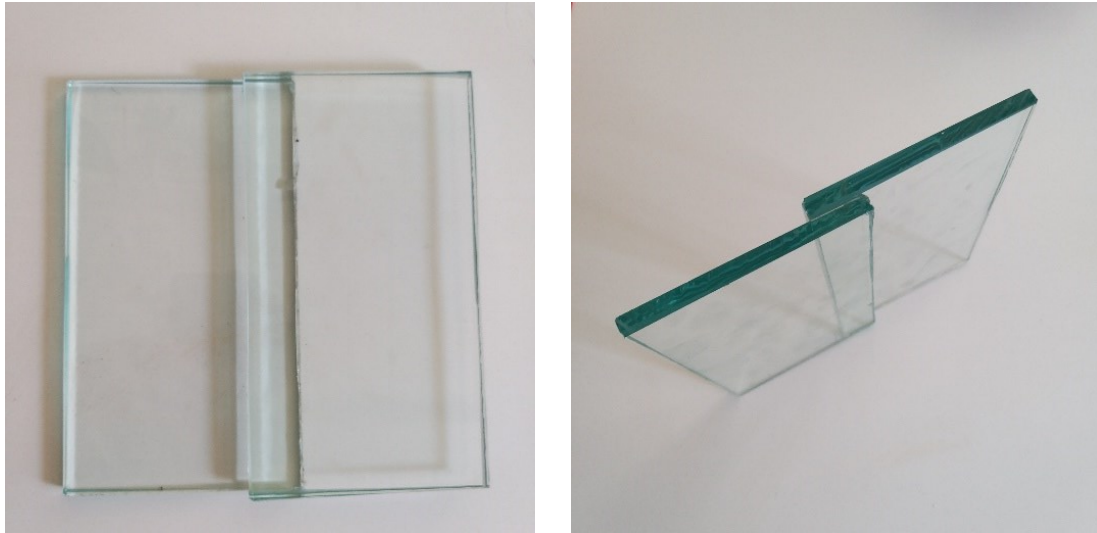


Figure 3.16 Specimen for single-lap shear test

Prior to testing, all specimens were marked with a row of black dots, used for optical elongation measurement, and wrapped in adhesive tape to prevent glass splinter projection after the breakage of the specimen.

The single-lap shear tests were performed at room temperature. Each specimen, inserted in an ad hoc steel plate, was placed in the grips, taking care to align the longitudinal axis of the test specimen with the axis of the testing machine (Zwisch Roell Z050 with a 50'000 N load cell). The grips were tightened evenly and firmly to prevent slippage of the test specimen and movement of the grips during the test.

After placing the test specimen, two cameras (Pixelink PL-B) for optical elongation measurement were set up and adjusted. An elongation rate of 2 mm/min was set (in this thesis the time dependence of the laminated glass mechanical properties is not studied).

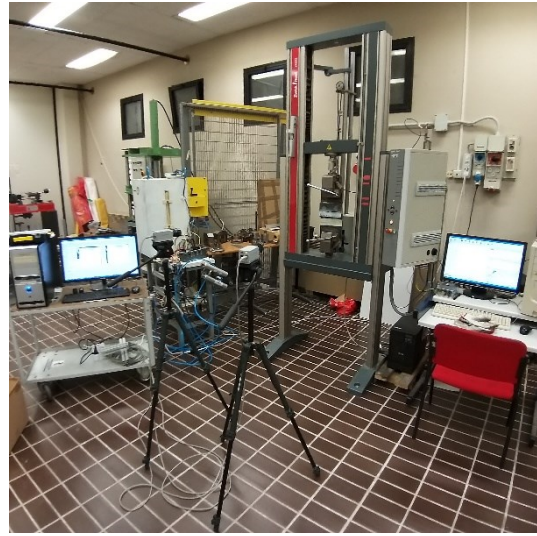
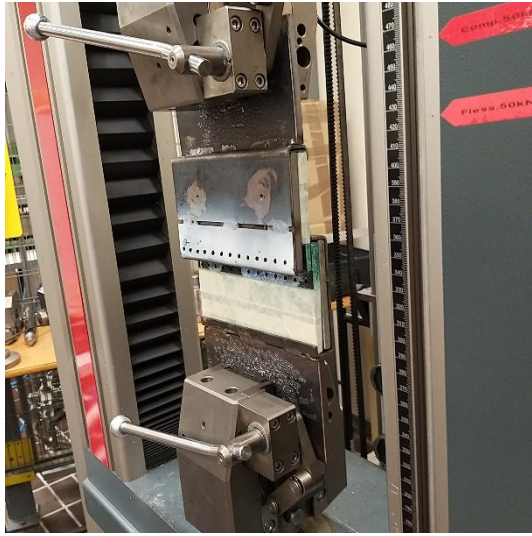


Figure 3.17 Setup for single-lap shear test

The rupture, as shown in following Figure 3.18 and Figure 3.19, was almost always an adhesive failure with detachment of a monolithic glass from the PVB. In two cases there was a mixed failure with prevalence of adhesive failure and a small cohesive failure of the substrate confined to a corner.

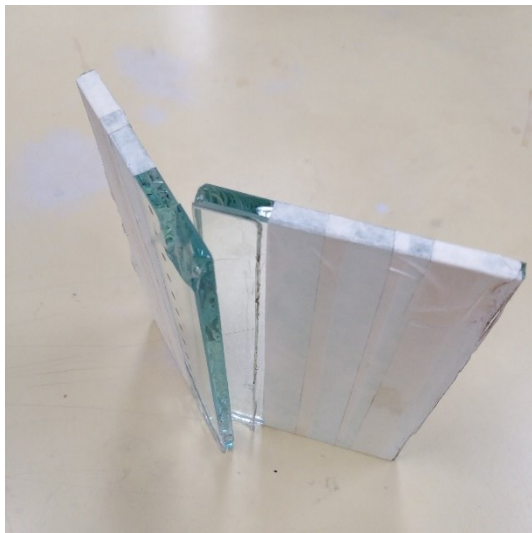


Figure 3.18 Adhesive failure with detachment of a monolithic glass from the PVB

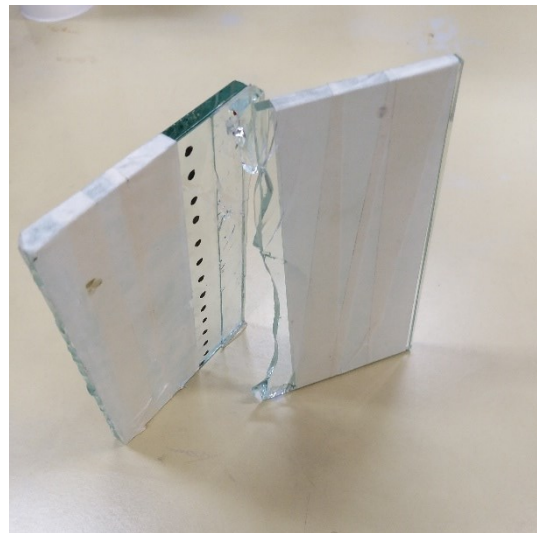


Figure 3.19 Mixed failure with prevalence of adhesive failure and a small cohesive failure

3.5 Ageing Test

Ageing test was carried out according to UNI EN ISO 12543-4 [21].

The ageing test regards:

- Five (5) test specimens which will be used for “*Tensile Test*”, 25 x 190 mm obtained by cutting them from a larger PVB sheet with a cutter. Particular care was taken to avoid any contamination;
- Five (5) test specimens which will be used for “*Single-Lap Shear Test*”, obtained as explained in chapter 3.4.

First step of this test was to keep the test specimens for two weeks in an upright position in a climatic chamber at $50\text{ °C} \pm 5\text{ °C}$ and $80\% \pm 5\% \text{ RH}$. An adequate separation between the test specimens was ensured. These specific parameters were maintained through the use of a humidifier and an electric heater. Osmotic water was used to prevent any contamination of the specimens.

Second step was to carry out the *Tensile Test* explained in the chapter 3.3 and the *Single-Lap Shear Test* explained in the chapter 3.4.



Figure 3.20 Setup for ageing test

3.6 UV-Vis Test

UV-Vis Test was carried out according to UNI EN 410:2011 [22].

Three (3) test specimens (for each type of PVB), used in this test, were obtained by bounding two 3 mm monolithic pieces of clear glass 40 x 40 mm with PVB. The composition of the laminated glass was: 3 mm clear glass + PVB + 3 mm clear glass. The sandwiches were obtained with a lamination process carried out in Nova Vetro S.r.l in an autoclave for 4 hours at a fixed temperature of 128 °C and a pressure of 7 bar.

Spectrophotometry

Spectrophotometry is a branch of electromagnetic spectroscopy concerned with the quantitative measurement of the reflection or transmission properties of a material as a function of wavelength [28].

Spectrophotometers use a monochromator containing a diffraction grating to produce the analytical spectrum. The grating can either be movable or fixed. If a single detector, such as a photomultiplier tube or photodiode is used, the grating can be scanned stepwise (scanning spectrophotometer) so that the detector can measure the light intensity at each wavelength (which will correspond to each "step") [28].

When making transmission measurements, the spectrophotometer quantitatively compares the fraction of light that passes through a reference solution and a test solution, then electronically compares the intensities of the two signals and computes the percentage of transmission of the sample compared to the reference standard. For reflectance measurements, the spectrophotometer quantitatively compares the fraction of light that reflects from the reference and test samples. Light from the source lamp is passed through a monochromator, which diffracts the light into a "rainbow" of wavelengths through a rotating prism and outputs narrow bandwidths of this diffracted spectrum through a mechanical slit on the output side of the monochromator. These bandwidths are transmitted through the test sample. Then the photon flux density (watts per meter squared usually) of the transmitted or reflected light is measured with a photodiode, charge coupled device or another light sensor. The transmittance or reflectance value for each wavelength of the test sample is then compared with the transmission or reflectance values from the reference sample [28].

In short, the sequence of events in a scanning spectrophotometer is as follows (Figure 3.21) [28]:

1. The light source is shone into a monochromator, diffracted into a rainbow, and split into two beams. It is then scanned through the sample and the reference solutions;
2. Fractions of the incident wavelengths are transmitted through, or reflected from, the sample and the reference;
3. The resultant light strikes the photodetector device, which compares the relative intensity of the two beams;
4. Electronic circuits convert the relative currents into linear transmission percentages and/or absorbance/concentration values.

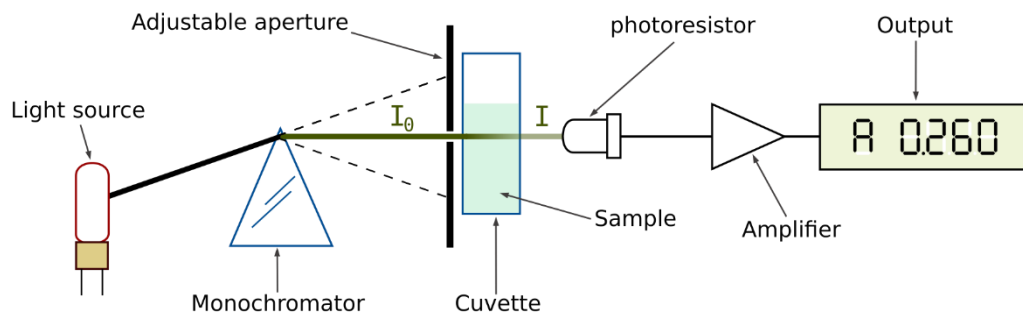


Figure 3.21 Single beam scanning spectrophotometer [28]

The UV-Vis tests were performed using the Jasco® V-670 UV-Vis / NIR spectrophotometer which uses a single beam to measure the relative light intensity of the beam before and after placing a specimen over a range of wavelength from 280 nm to 2700 nm.

Chapter 4

Results and Discussion

The performance of a composite material like laminated glass depends on the properties of each one of the materials and the interaction between them. It is important to evaluate the mechanical properties of the interlayer material in laminated glass plates because it will affect its global structural response.

4.1 Water Absorption Test

Standard PVB

Figure 4.1 shows the mass increase of standard PVB due to water absorbed as a function of immersion time. The overall increase in weight up to 216 hours ($m_{10/216h}$) by PVB-1, PVB-2 and PVB-3 was 5.082%, 5.125%, and 5.109% respectively (see Figure 4.2). The water absorption was much higher at the beginning of the test: standard PVB achieved 98% of the total mass increase during the first 24 h of immersion (11% of the total duration). At $m_{2/24h}$, increase in weight due to water absorption by PVB-1, PVB-2 and PVB-3 was recorded 3.678%, 3.763%, and 3.798%. Starting from $m_{6/120h}$ to $m_{10/216h}$ there was almost no water absorption by the standard PVB specimens.

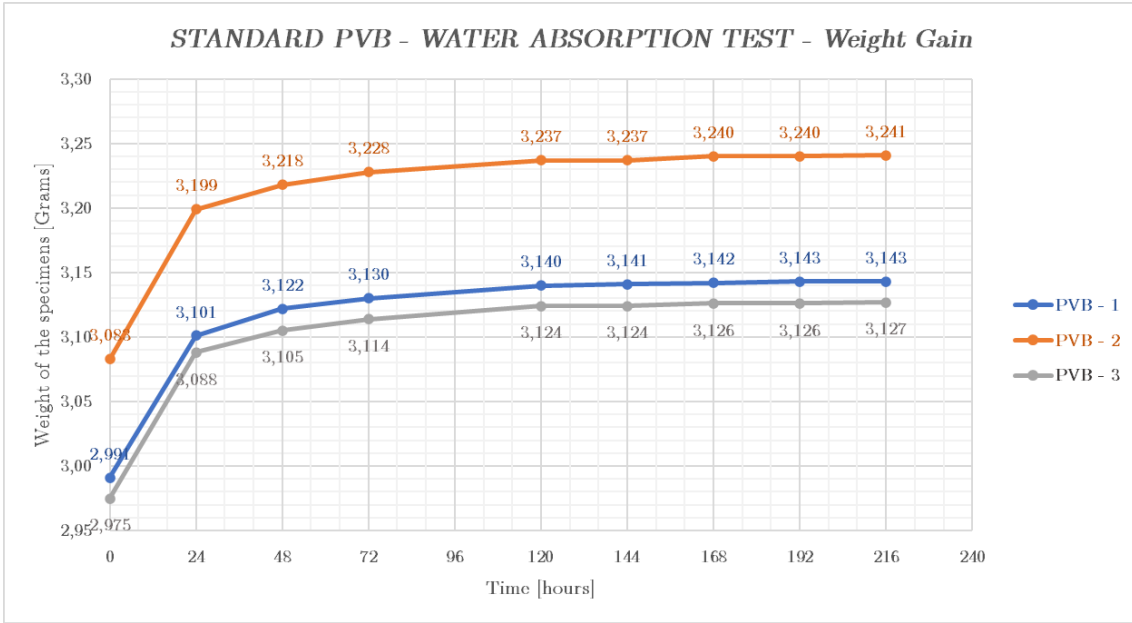


Figure 4.1 Change in the weight of the standard PVB specimens was compared in time interval (each 24 hours till 216 hours)

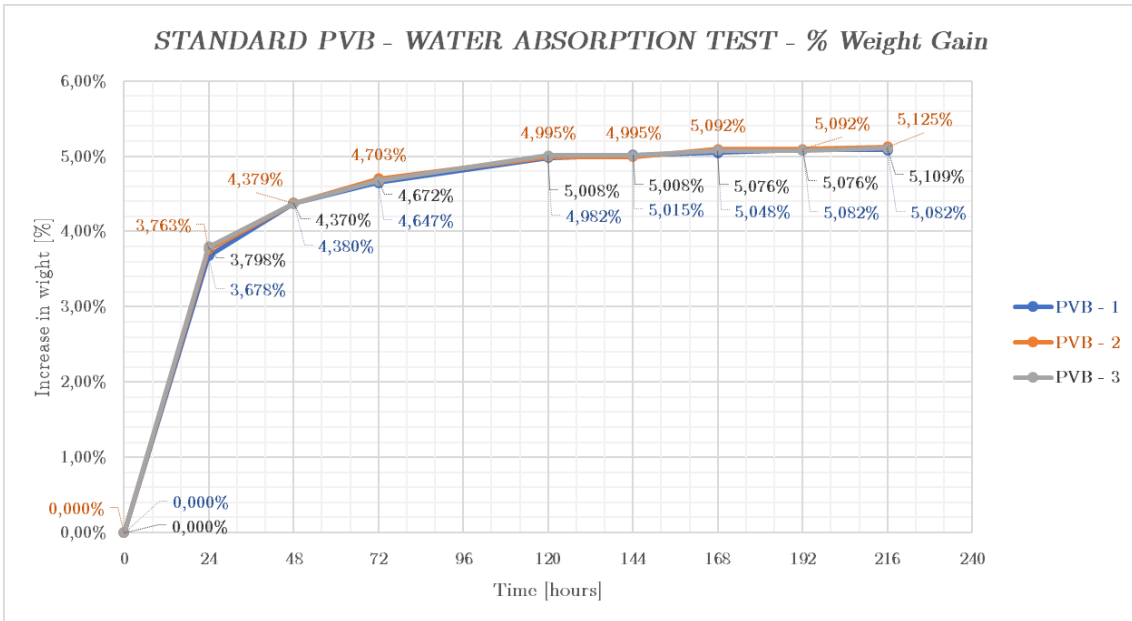


Figure 4.2 Mass increase (%) over time (hours) for the three standard PVB specimens immersed in distilled water

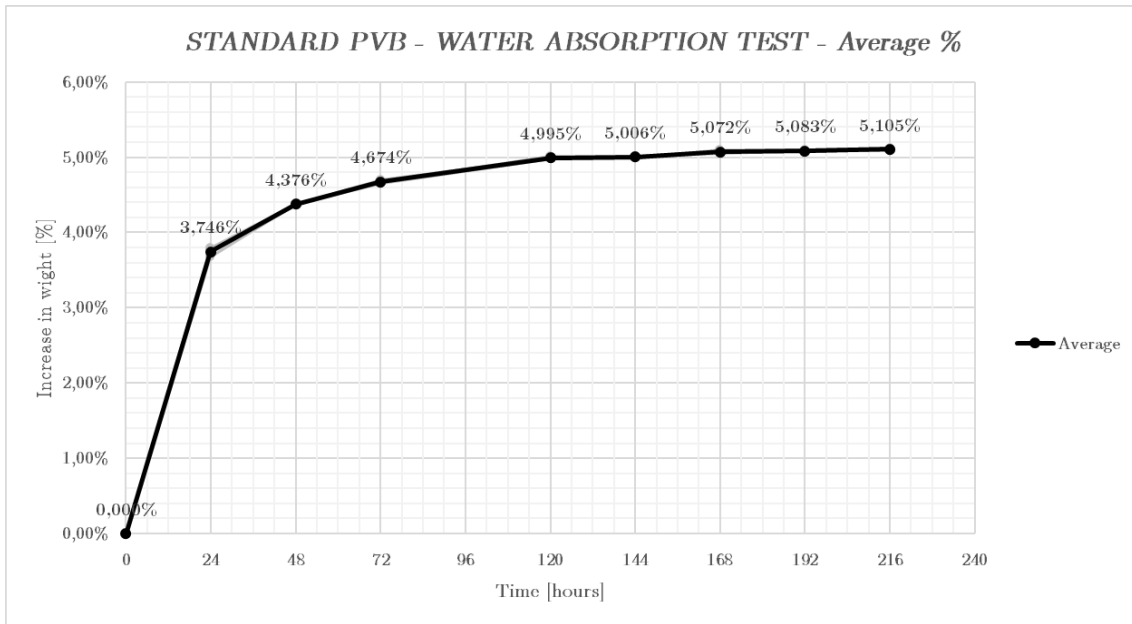


Figure 4.3 Average mass increase (%) over time (hours) for the three standard PVB specimens

An interlayer is able to absorb more or less water depending on the chemical nature of the polymer. Polymers with strong polar groups are able to bind water by hydrogen bridges and therefore be more sensitive to water exposure. For instance, interlayer materials based on PVB, due to its significant proportion of polar alcohol groups, are hygroscopic materials, which easily increase the water content.

Figure 4.4 compares the results (average mass increase %) obtained in this research and the results available in the literature. The trend of the mass increase is the same as for the other PVBs, especially in the first 96 hours. There is a small difference after 120 hours (4.995% for “Standard PVB” and 5.560% for “PVB ES” due to the different type of PVB analyzed and its chemical composition: Saflex® Clear PVB by Eastman used in this thesis and Trosifol® Clear PVB by Kuraray used in the literature.

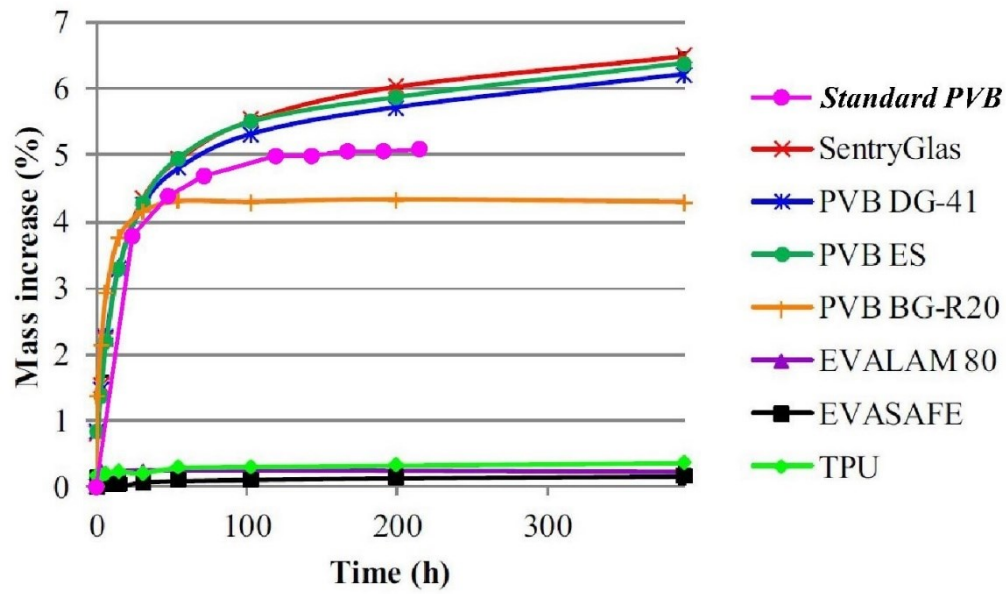


Figure 4.4 Comparison of result [23]

Nano-net PVB

Figure 4.5 shows the mass increase of nano-net PVB due to water absorbed as a function of immersion time. The overall increase in weight up to 264 hours ($m_{12/264h}$) by PVB-1, PVB-2 and PVB-3 was 14.666%, 13.380%, and 13.875% respectively (see Figure 4.6). The water absorption was much higher at the beginning of the test: nano-net PVB achieved 62% of the total mass increase during the first 24 h of immersion (9% of the total duration). At $m_{2/24h}$, increase in weight due to water absorption by PVB-1, PVB-2 and PVB-3 was recorded 9.256%, 7.515%, and 9.192%. Starting from $m_{2/24h}$ to $m_{11/240h}$ there was a constant weight gain in percentage and from $m_{11/240h}$ there was almost no water absorption by the nano-net PVB specimens.

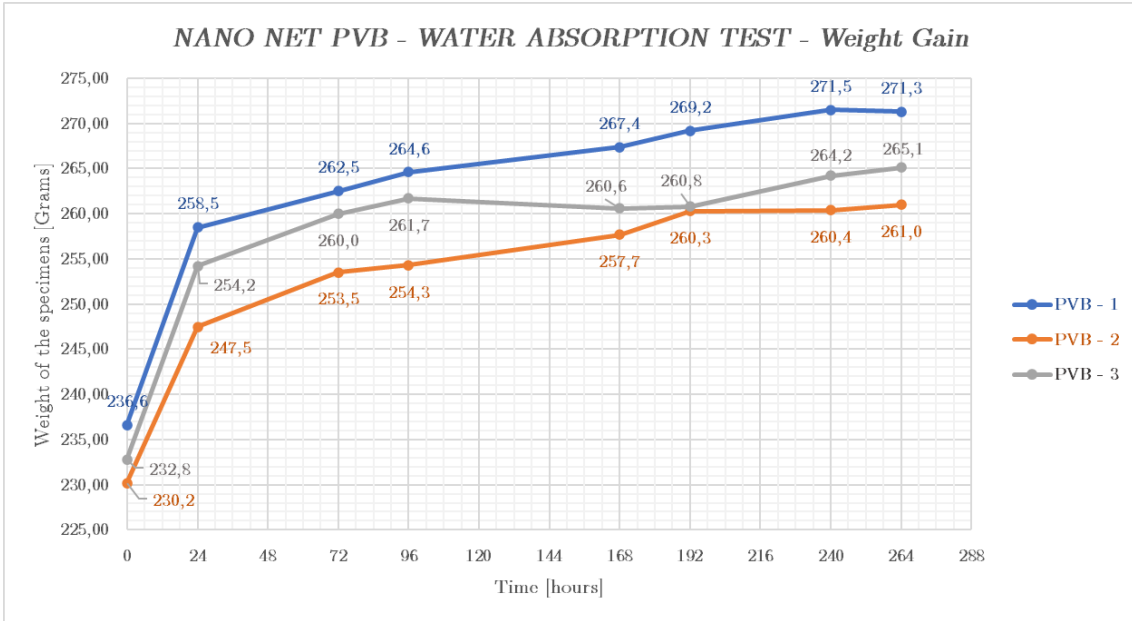


Figure 4.5 Change in the weight of the nano-net PVB specimens was compared in time interval (each 24 hours till 264 hours)

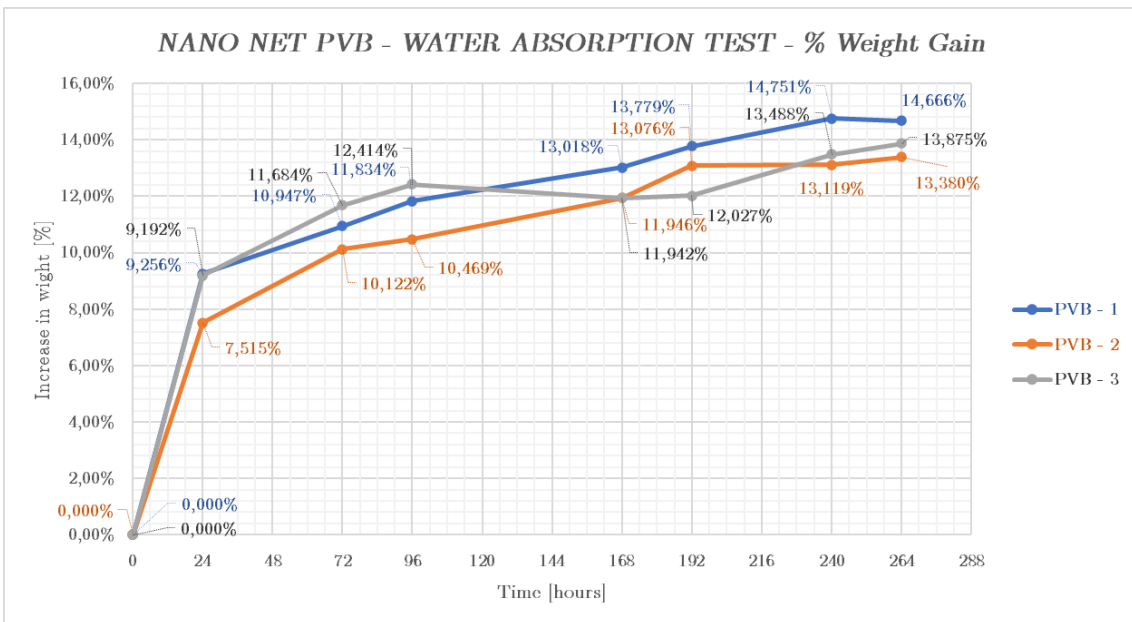


Figure 4.6 Mass increase (%) over time (hours) for the three nano-net PVB specimens immersed in distilled water

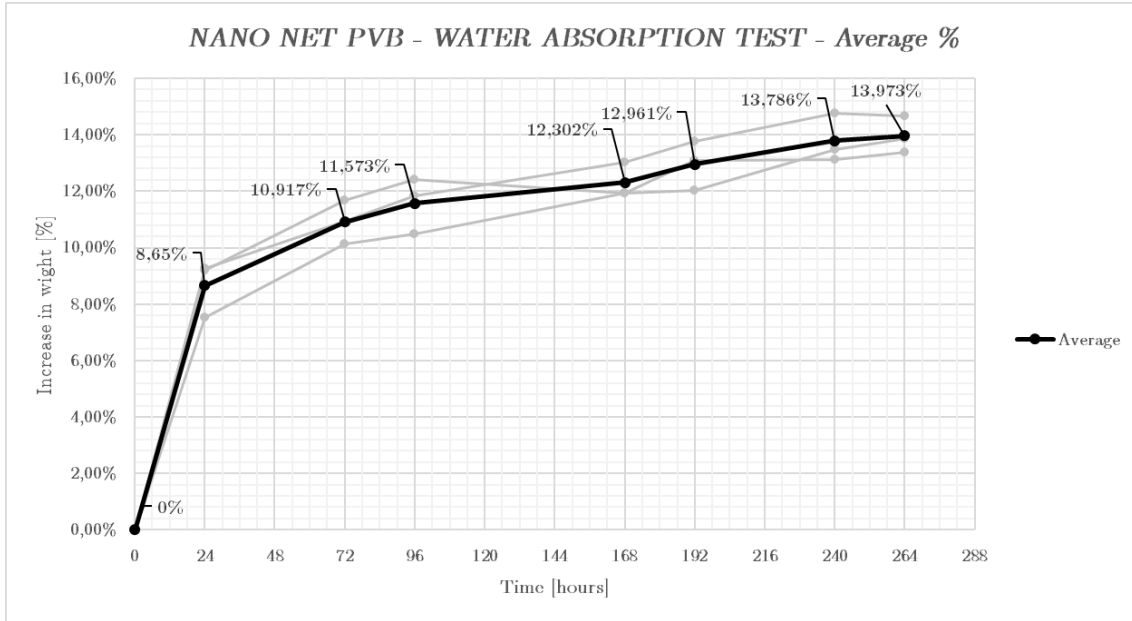


Figure 4.7 Average mass increase (%) over time (hours) for the three nano-net PVB specimens

Comparison

Figure 4.8 compares the results (average mass increase %) obtained in water absorption test of standard PVB and nano-net PVB. The trend of the mass increase is almost the same for both type of PVB, especially in the first 72 hours. There is a difference after 96 hours as the standard PVB no longer has water absorption while the nano-net PVB continues to increase its weight up to 240 hours. This phenomenon, in the nano-net PVB, is due both to the fact that it is a hygroscopic material and to the presence of voids between the fibers of the nano-web that are slowly occupied by the water molecules. In terms of percentage values, the water absorption in these two materials, are clearly different: the nano-net PVB absorbs water, after 24 hours, about 2.3 times more than the standard PVB and, after 216 hours, about 2.7 times. The recorded values are respectively 8,655% (24 hours) and 13,374% (216 hours) for the nano-net PVB and 3,746% (24 hours) and 5,105% (216 hours) for the standard PVB.

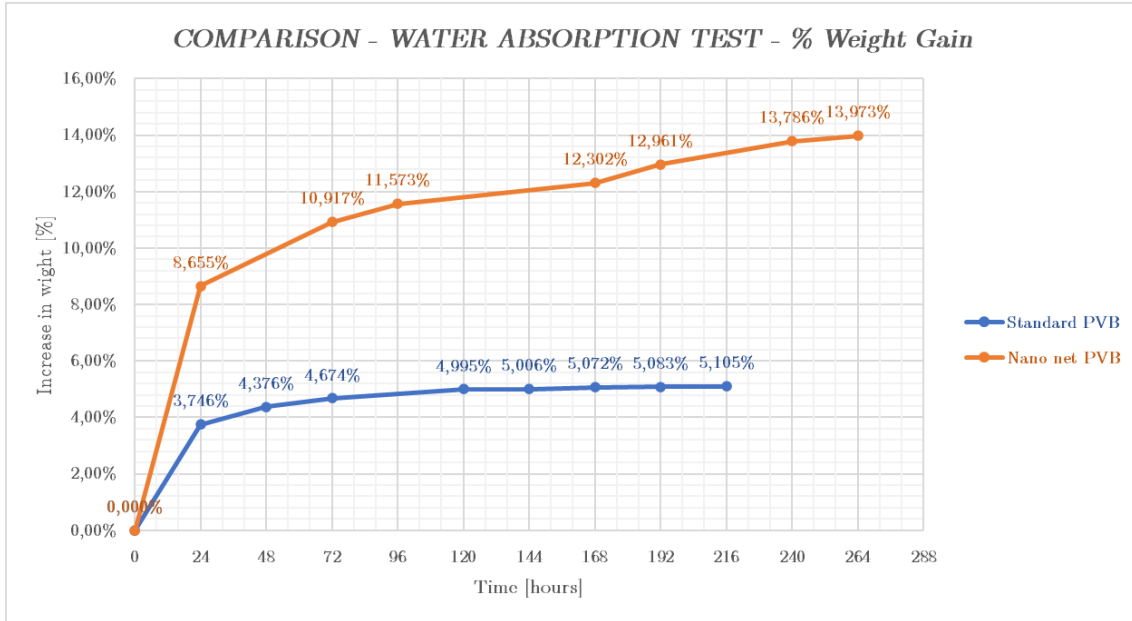


Figure 4.8 Comparison of result

This trend, by the nano-net PVB, to absorb more water and humidity, compared to standard PVB, can lead to the occurrence of a known phenomenon as “delamination”.

The delamination process of a laminated glass sheet is the phenomenon that occurs at the exposed edges of the sheet and consists in the loss of adhesion between the glass sheets and the plastic interlayer film (in this case PVB) that holds them normally combined. The main causes of the phenomenon include an excessively hot and humid atmosphere (the PVB is hygroscopic), compatibility problems between the plastic interlayer and the structural silicone (if used), incorrect management of the lamination process, installation conditions (presence of substances that can attack the interlayer and its adhesion to the glass). The phenomenon does not only concern glass of curtain walls but it can affect glass of parapets (Figure 4.9) or more simply glass of windows (Figure 4.10). Delamination is also known in the automotive field.



Figure 4.9 Delamination phenomenon around a parapet hole



Figure 4.10 Delamination in an Insulated Glass Unit

4.2 Tensile Test

Stress-strain diagrams can be produced by various approaches. The stress and strains can be calculated either as true stress/strain or engineering stress/strain. True stress and true strain are based upon instantaneous values of cross-sectional area and gage length. Engineering stress is calculated from

$$\sigma = \frac{F}{A}$$

where F is the applied load and A is the cross-sectional area. The engineering strain is calculated from

$$\varepsilon = \frac{\Delta L}{L} = \frac{l - L}{L}$$

where ε is the engineering strain, L is the original length and l is the final length of the specimen. The length was measured with the camera. By using two equations shown previously a stress-strain diagram can be produced.

Standard PVB

Results were plotted in the stress-strain diagram (Figure 4.11), representing stress as the ratio of the applied load to the initial cross section, engineering strain as the ratio of the total deformation to the initial specimen length and toughness as the area under the stress-strain curve. The deformation was obtained by converting the video, captured by the camera, into numerical values using the program MATLAB. For this test, six specimens were tested; a mean value curve (Figure 4.12) and a mean value table, which is presented in Table 4.1, were created.

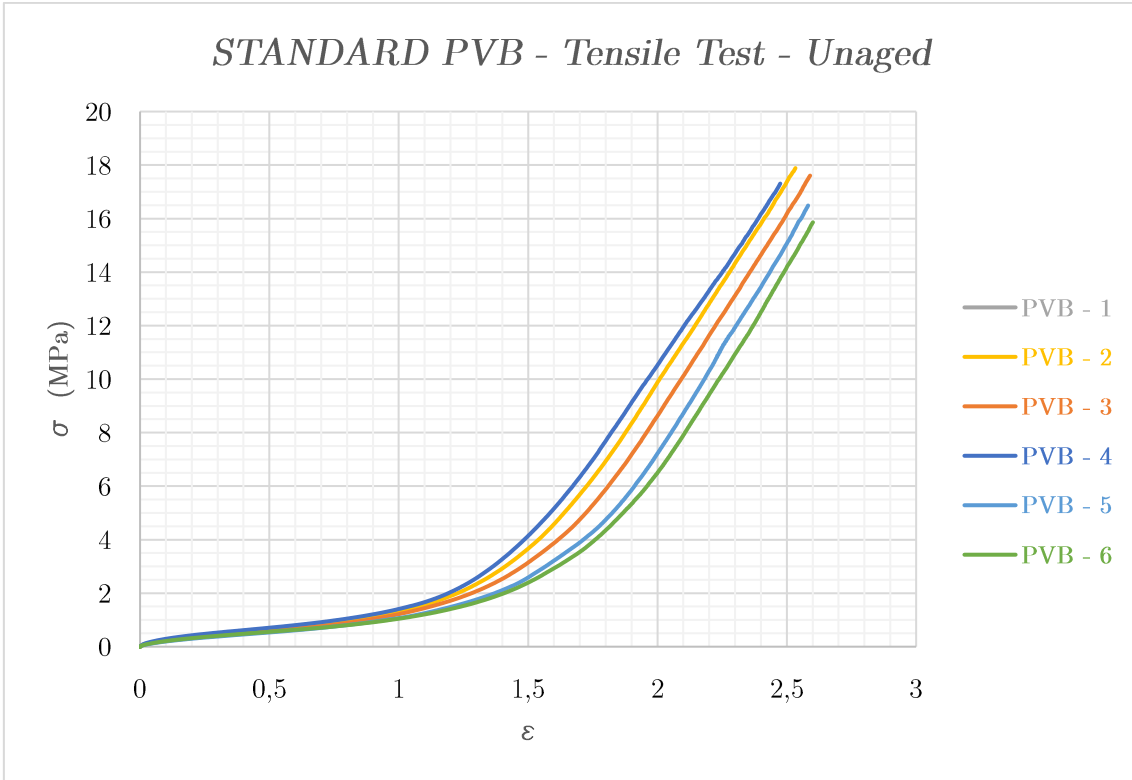


Figure 4.11 Stress-strain diagram of unaged standard PVB

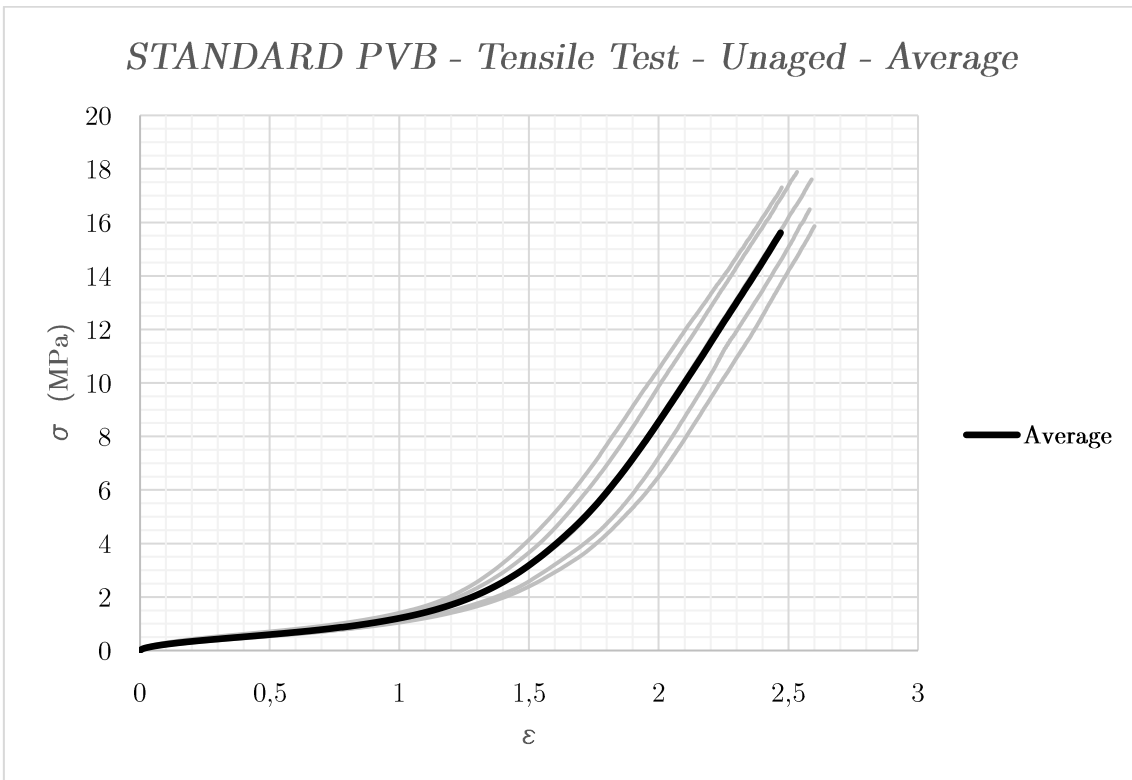


Figure 4.12 Average stress-strain diagram of unaged standard PVB

Table 4.1 Mean value of unaged standard PVB tensile test

Standard PVB - Unaged			
	σ_R (MPa)	E (MPa)	ν
PVB - 1	18,61	9,99	0,4287
PVB - 2	17,95	8,38	-
PVB - 3	17,64	7,91	-
PVB - 4	17,38	11,05	0,4528
PVB - 5	16,55	7,12	0,4791
PVB - 6	15,88	8,11	0,4516
Average	17,34	8,76	0,4531
St. Dev.	0,98	1,46	0,0206
σ^*	5,66%	16,70%	4,55%

As shown in the previous curves, the mechanical behavior of the PVB, under tensile stress, is a hyperelastic behavior, whose stress-strain relationship can be defined as non-linearly elastic, isotropic, incompressible and dependent on the strain rate. The most common example of this type of material is rubber, the chemical composition of which is similar to the studied PVB.

The elongation at failure for PVB-2, PVB-3, PVB-4, PVB-5 and PVB-6 was 253%, 259%, 247%, 258% and 260% respectively while the tensile strength was 17.89 MPa, 17.61 MPa, 17.31 MPa, 16.49 MPa and 15.86 MPa respectively. The tensile strength was much lower at the beginning of the test: PVB achieved 12% of the maximum tensile strength during the first half of elongation (50% of the total duration).

Nano-net PVB

Results were plotted in the stress-strain diagram (Figure 4.13), representing stress as the ratio of the applied load to the initial cross section, engineering strain as the ratio of the total deformation to the initial specimen length and toughness as the area under the stress-strain curve. The deformation was obtained by converting the video, captured by the camera, into numerical values using the program MATLAB. For this test, two specimens were tested; a mean value curve (Figure 4.14) and a mean value table, which is presented in Table 4.2, were created.

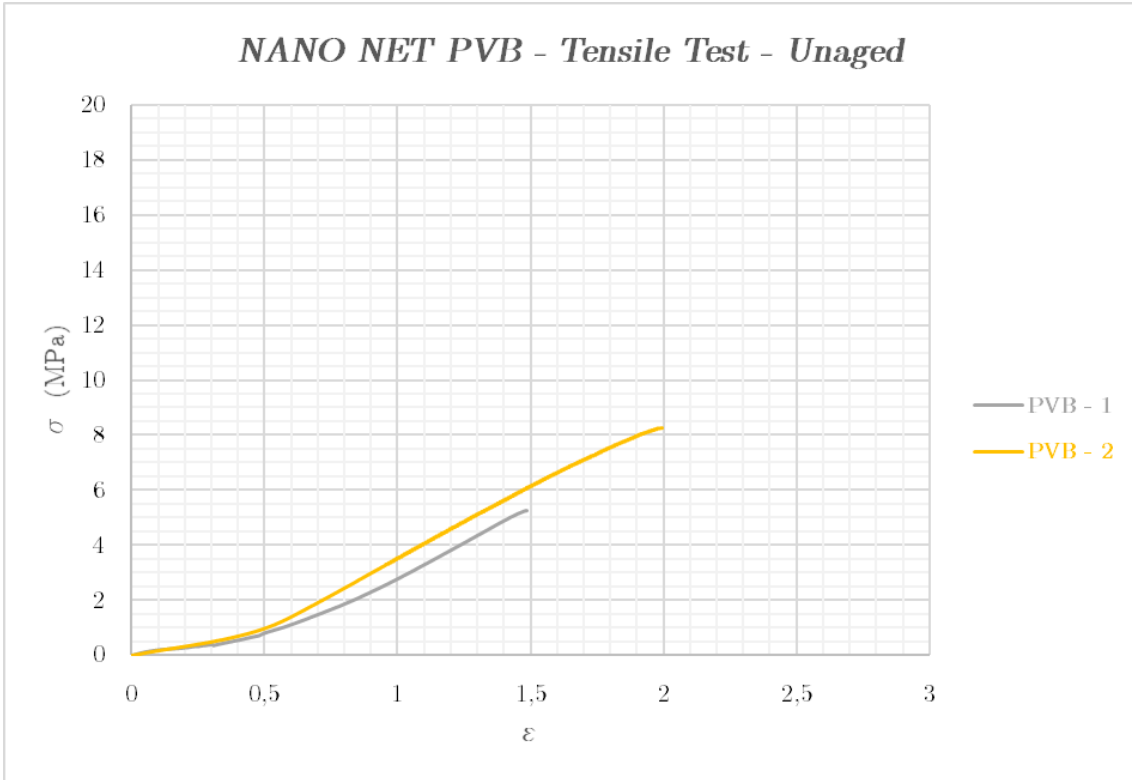


Figure 4.13 Stress-strain diagram of unaged nano-net PVB

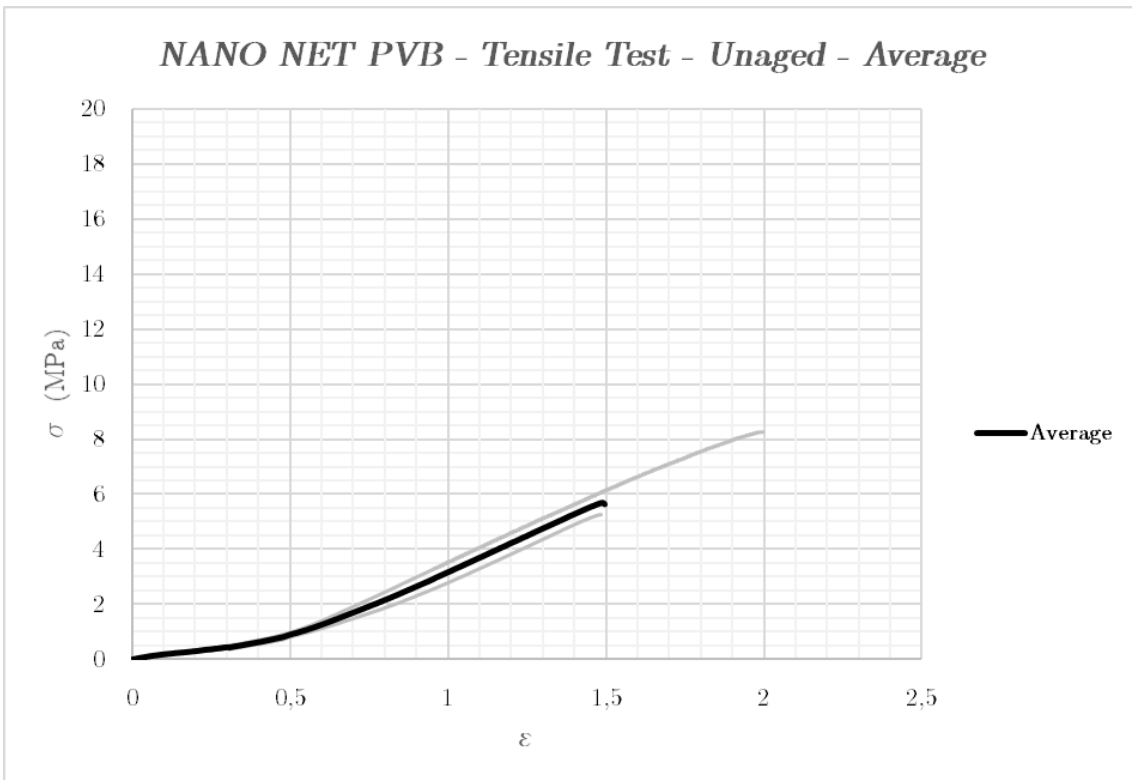


Figure 4.14 Average stress-strain diagram of unaged nano-net PVB

Table 4.2 Mean value of unaged nano-net PVB tensile test

Nano-net PVB - Unaged			
	σ_R (MPa)	E (MPa)	ϵ_R (%)
PVB - 1	5,24	3,15	150
PVB - 2	8,27	1,81	201
Average	6,75	2,48	175
St. Dev	2,14	0,95	35,96
σ^*	31,72%	38,17%	20,53%

As shown in the previous curves, nano-net PVB maintains the same hyperelastic mechanical behavior of the standard PVB under tensile stress.

The elongation at failure for PVB-1 and PVB-2 was 150% and 201% respectively while the tensile strength was 5.24 MPa and 8.27 MPa respectively. The tensile strength was much lower at the beginning of the test: PVB achieved 13% of the maximum tensile strength during the early stages of elongation (25% of the total duration). After 50% of the specimen elongation, the stress-strain diagram shows a constant linear increase in slope until failure.

Comparison

The stress-strain diagram of the standard PVB was combined with that of the nano-net PVB and shown in Figure 4.15. In this way, a well-defined overview of the differences between the performance of these two materials was obtained.



Figure 4.15 Comparison between average stress-strain diagram of unaged standard PVB and nano-net PVB

Comparing the average values of the two materials, it can be seen that:

- Nano-net PVB has a mean elongation at failure 31.4% less than the standard PVB (respectively, 175% and 255%);
- The first material develops an average stress at failure less than 61.1% compared to the second (respectively, 6.75 MPa and 17.34 MPa);
- Nano-net PVB has a higher toughness up to about 200% of the total elongation of the specimen.

The performance of a composite material like laminated glass depends on the properties of each one of the materials and the interaction between them. For this reason, it is preferable to use the interlayer with higher mechanical properties.

The parameters that are considered more important for the implementation of the tested materials in laminated glass structural elements are toughness, maximum tensile stress, and initial stiffness. A higher toughness and maximum tensile stress are two key properties to increase the safety of laminated glass elements, because, in case of accidental glass breakage, the post-breakage load-bearing capacity of the interlayer allows the evacuation of civilians from the affected area and the replacement of the damaged elements. A higher initial stiffness leads to a higher

transfer of shear loads between two connected glass surfaces, providing smaller out-of-plane deflections and therefore a higher out-of-plane stability [23].

4.3 Single Lap-Shear Test

In order to evaluate the effect of PVB shape on the adhesion with the glass layers, a single lap-shear test was performed on both standard and nano-net PVB samples; the obtained data were then compared.

For each material two diagrams were drawn:

- A load-displacement diagram representing the recorded load as a function of the displacement of the crosshead of the testing machine;
- A stress-strain diagram representing the mean stress τ as a function of the bond elongation γ

Where:

- γ was calculated through the use of two optical strain gauges;
- τ was calculated as the ratio between the load applied and the area of the bond

$$\tau = \frac{F}{A}$$

where the bond was 20 mm wide and 180 mm high

Standard PVB

The results were plotted in the load-displacement diagram (Figure 4.16) and in the stress-strain diagram (Figure 4.17). The mean values are summarized in Table 4.3.

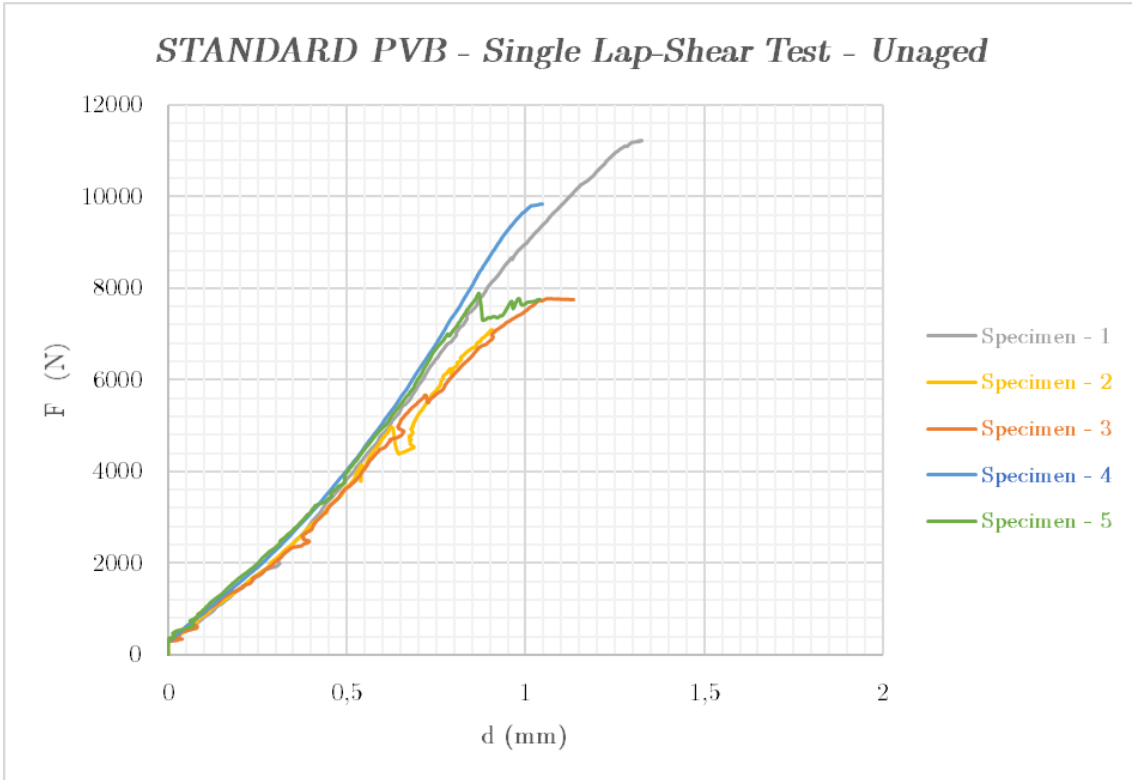


Figure 4.16 Load-displacement diagram of unaged standard PVB

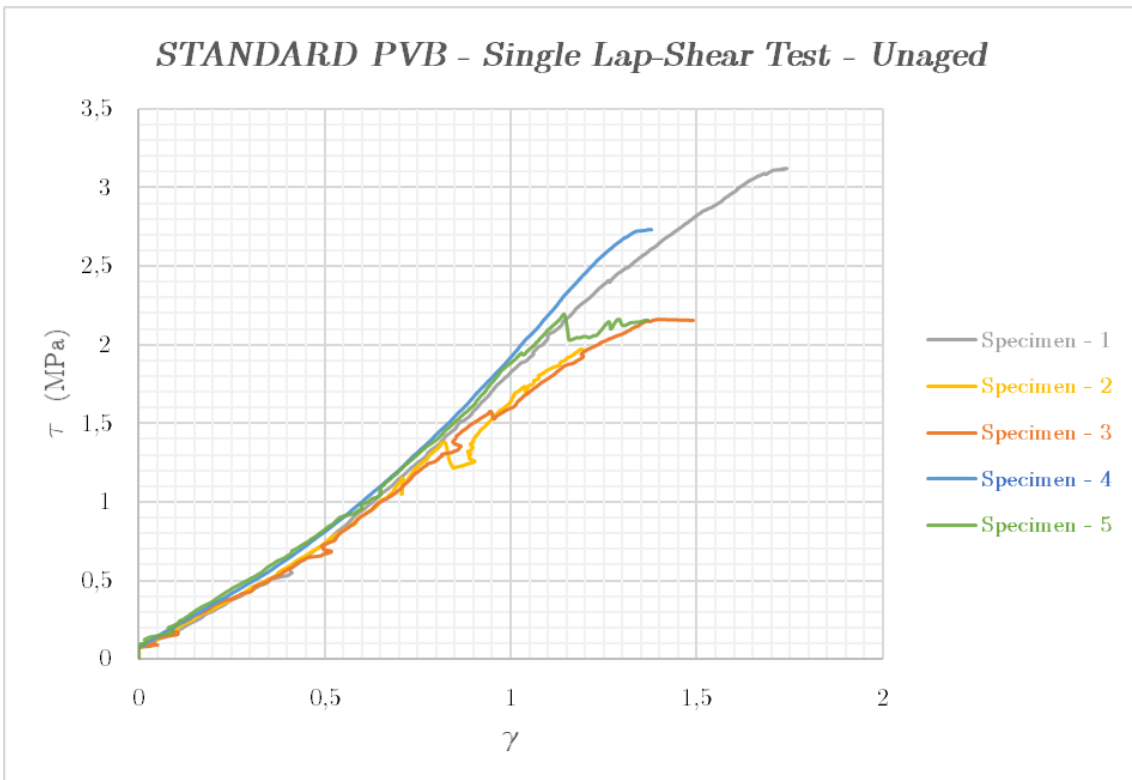


Figure 4.17 Stress-strain diagram of unaged standard PVB

Table 4.3 Mean value of unaged standard PVB single lap-shear test

Standard PVB - Unaged				
	F_{\max} (N)	K (N/mm)	τ_{\max} (MPa)	G (MPa)
PVB - 1	11232	7700	3,12	1,63
PVB - 2	7096	6163	1,97	1,30
PVB - 3	7778	6706	2,16	1,42
PVB - 4	9837	7264	2,73	1,53
PVB - 5	7895	6882	2,19	1,45
Average	8768	6943	2,44	1,47
St. Dev	1714	580	0,48	0,12
σ^*	19,55%	8,35%	19,55%	8,35%

Nano-net PVB

The results were plotted in the load-displacement diagram (Figure 4.18) and in the stress-strain diagram (Figure 4.19). The mean values are summarized in Table 4.4.

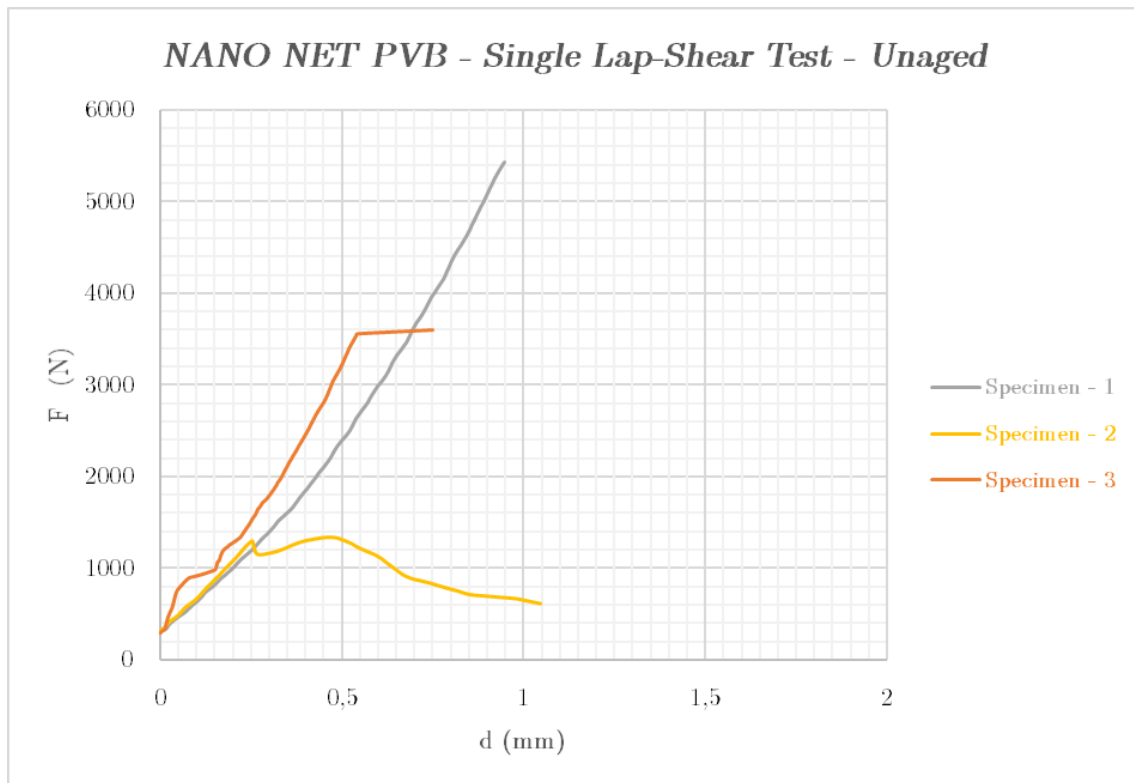


Figure 4.18 Load-displacement diagram of unaged nano-net PVB

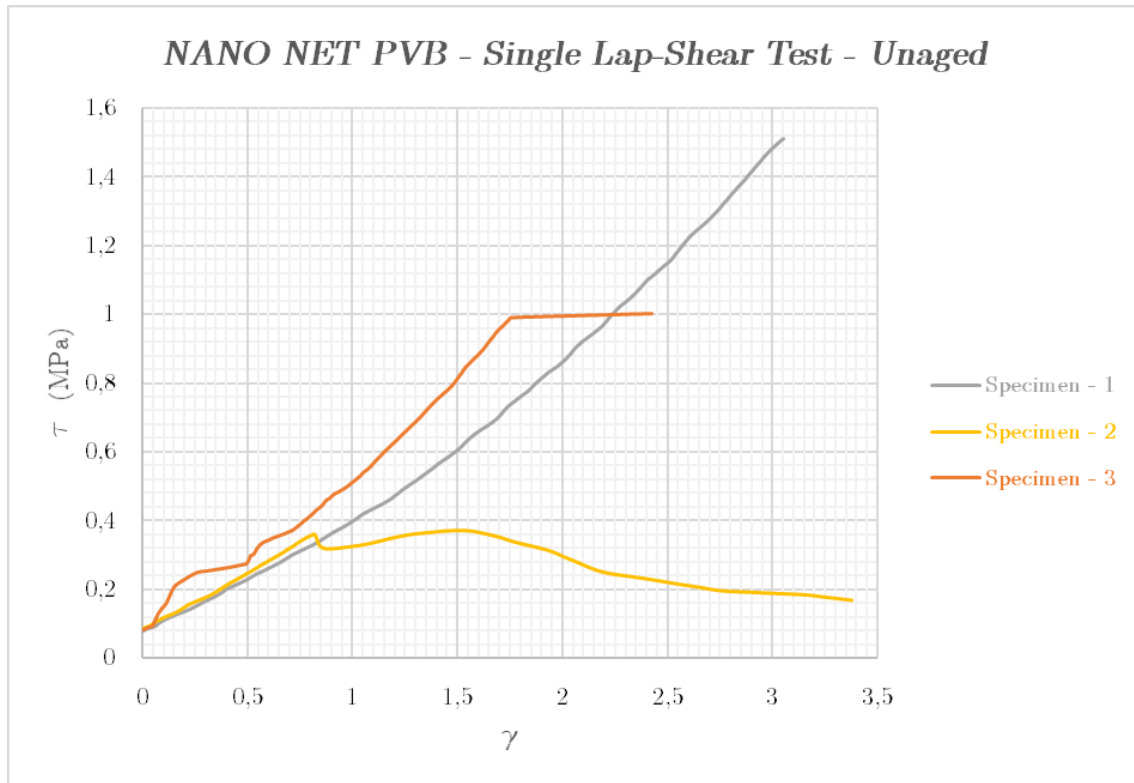


Figure 4.19 Stress-strain diagram of unaged nano-net PVB

Table 4.4 Mean value of unaged nano-net PVB single lap-shear test

Nano-net PVB - Unaged				
	F_{\max} (N)	K (N/mm)	τ_{\max} (MPa)	G (MPa)
PVB - 1	5433	4225	1,51	0,36
PVB - 2	1341	3707	0,37	0,32
PVB - 3	3646	5034	1,01	0,43
Average	3473	4322	0,96	0,37
St. Dev	2052	669	0,57	0,06
σ^*	59,06%	15,47%	59,06%	15,47%

Comparison

The load-displacement diagrams of the standard and nano-net PVBS were combined and shown in Figure 4.20. In this way, a well-defined overview of the differences between the performance of these two materials was obtained.

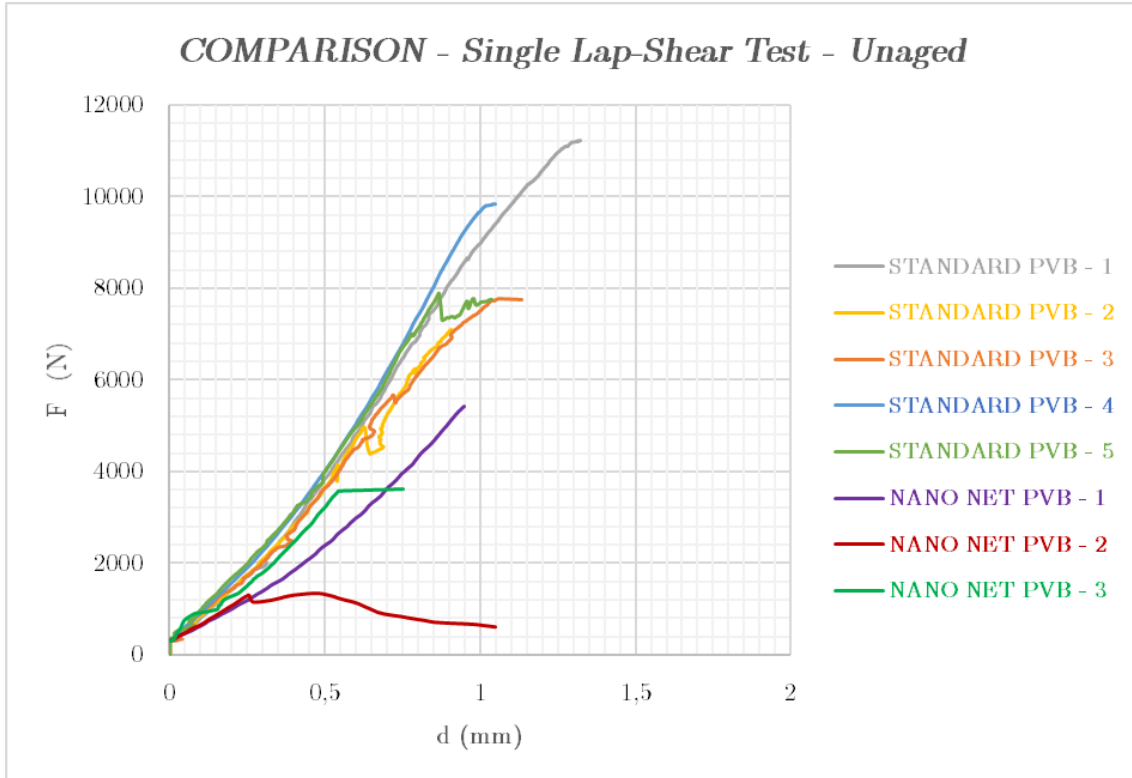


Figure 4.20 Comparison between load-displacement diagram of unaged standard PVB and nano-net PVB

The curve of the “NANO NET PVB – 2” has a completely different trend from the other specimens due to an incorrect lamination process which led to the formation of air bubbles inside the plastic, causing a considerable loss of performance.

The trend of the curves, relative to the other specimens, are almost similar. The nano-net PVB, however, achieves 51.8% lower breaking loads than the standard PVB (4.228 kN for the nano-net PVB and 8.768 kN for the standard PVB). This difference, in the behaviors of the two materials, is also present in terms of mean stress τ . In fact, the standard PVB reaches values of 2.44 MPa while the nano-net PVB achieves an average value of 1.26 MPa, showing a performance reduction of about 48.4%.

4.4 Ageing Test + Tensile Test

In the existing literature there are several studies carried out in order to evaluate the decay of the mechanical performance of PVB immersed in humid environments. The finding showed that water immersion had a negative effect on the stiffness and the ultimate tensile strength of the material that absorbed a great amount of water [23], due to its hygroscopicity.

Standard PVB

Results were plotted in the stress-strain diagram (Figure 4.21). For this test, five specimens were tested; the average curve and the mean values are respectively reported in Figure 4.22 and Table 4.5.

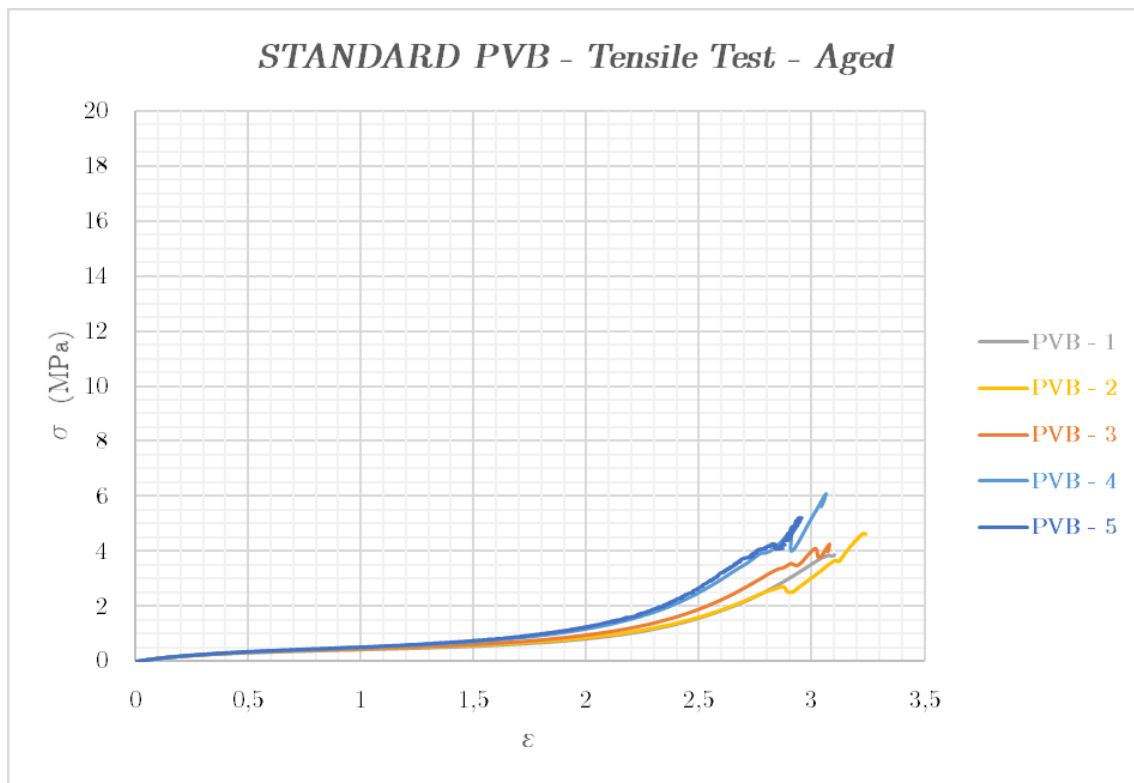


Figure 4.21 Stress-strain diagram of aged standard PVB

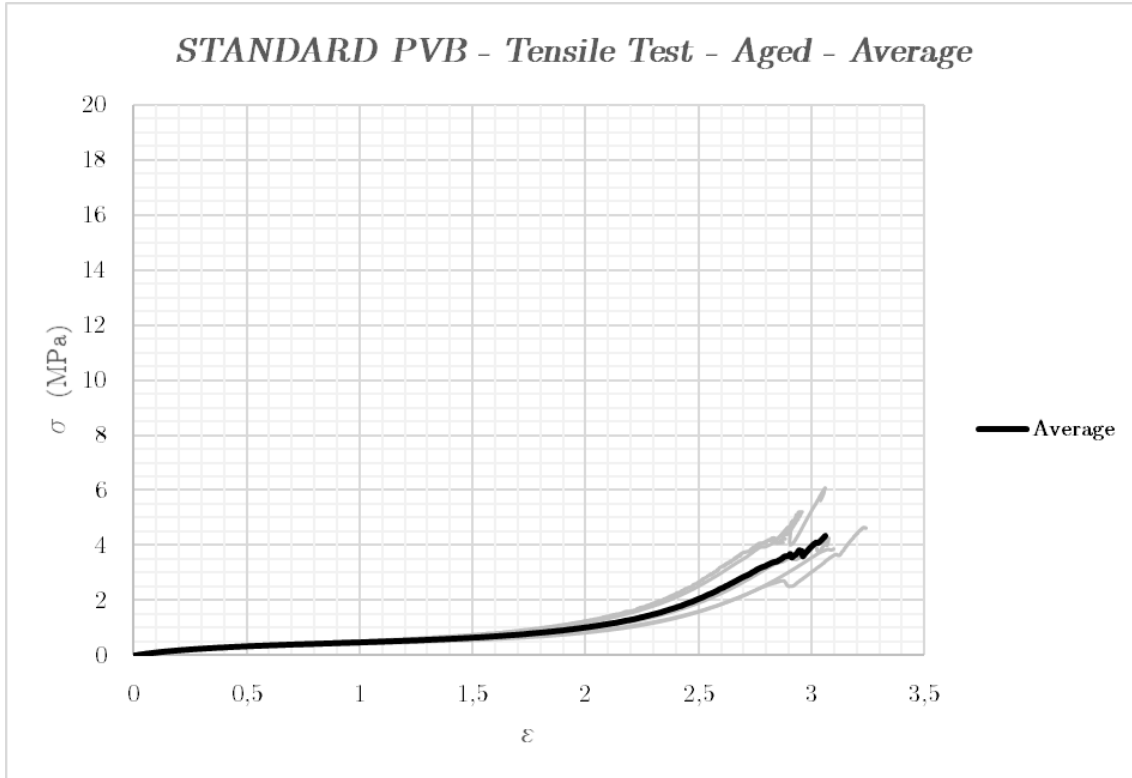


Figure 4.22 Average stress-strain diagram of aged standard PVB

Table 4.5 Mean value of aged standard PVB tensile test

Standard PVB - Aged				
	σ_R (MPa)	E (MPa)	ν	ϵ_R (%)
PVB - 1	3,87	1,50	0,4570	310
PVB - 2	4,64	1,56	0,4504	324
PVB - 3	4,26	1,27	0,4290	308
PVB - 4	6,10	1,23	0,4525	306
PVB - 5	5,20	1,16	0,4757	296
Average	4,82	1,34	0,4529	309
St. Dev	0,87	0,18	0,0167	10,18
σ^*	18,08%	13,16%	3,68%	3,30%

Figure 4.23 shows that water immersion decreases the toughness, maximum tensile stress, and initial stiffness of the standard PVB.

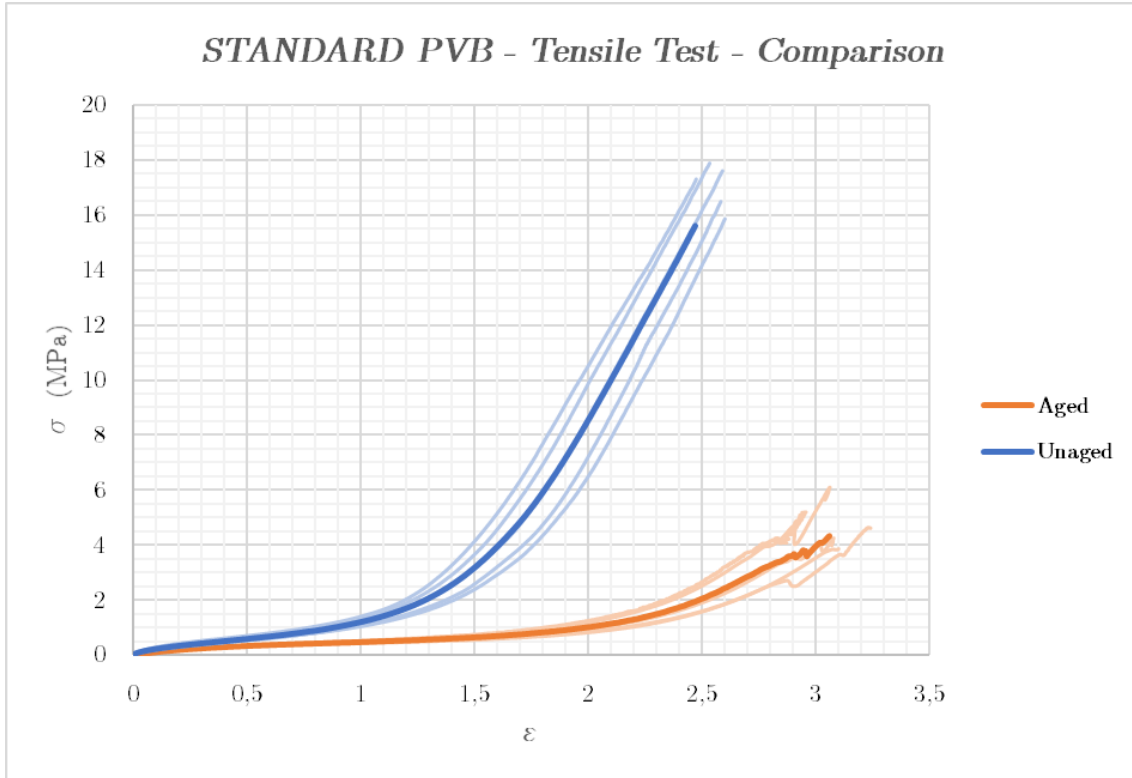


Figure 4.23 Comparison between average stress-strain diagram of unaged and aged standard PVB

The exposure of the standard PVB specimens under humid and hot environments, led to a 72.2% reduction in ultimate tensile stress (from 17.34 MPa to 4.82 MPa) and an increase of 21.2% in elongation at failure (from 255% to 309%). The ageing test also led to a significant decay on the toughness of the material.

Nano-net PVB

It was not possible to carry out the tensile test on the nano-net PVB specimens as they came out completely damaged after the ageing period of 14 days inside the climatic chamber. In detail: the specimens have completely lost their initial shape, the material contracted and concentrated more in a central circular area with a diameter of about 2 cm. Figure 4.24 shows the effects of ageing test on the specimens.

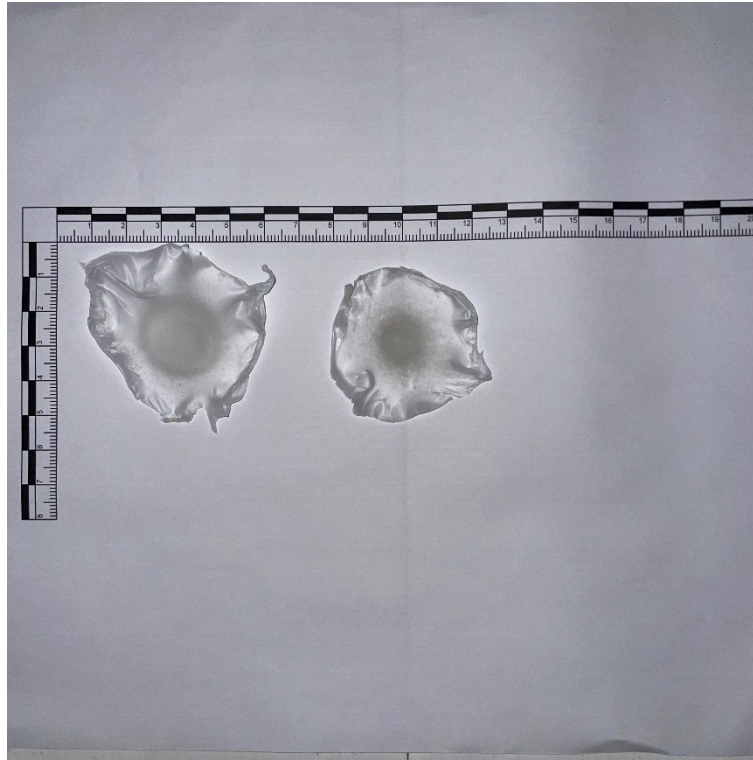


Figure 4.24 Specimens of PVB nano-net damaged after the ageing test

4.5 Ageing Test + Single Lap-Shear Test

Standard PVB

Results were plotted in the load-displacement diagram (Figure 4.25) and in the stress-strain diagram (Figure 4.26). For this test, five specimens were tested; the mean values are reported in Table 4.6.

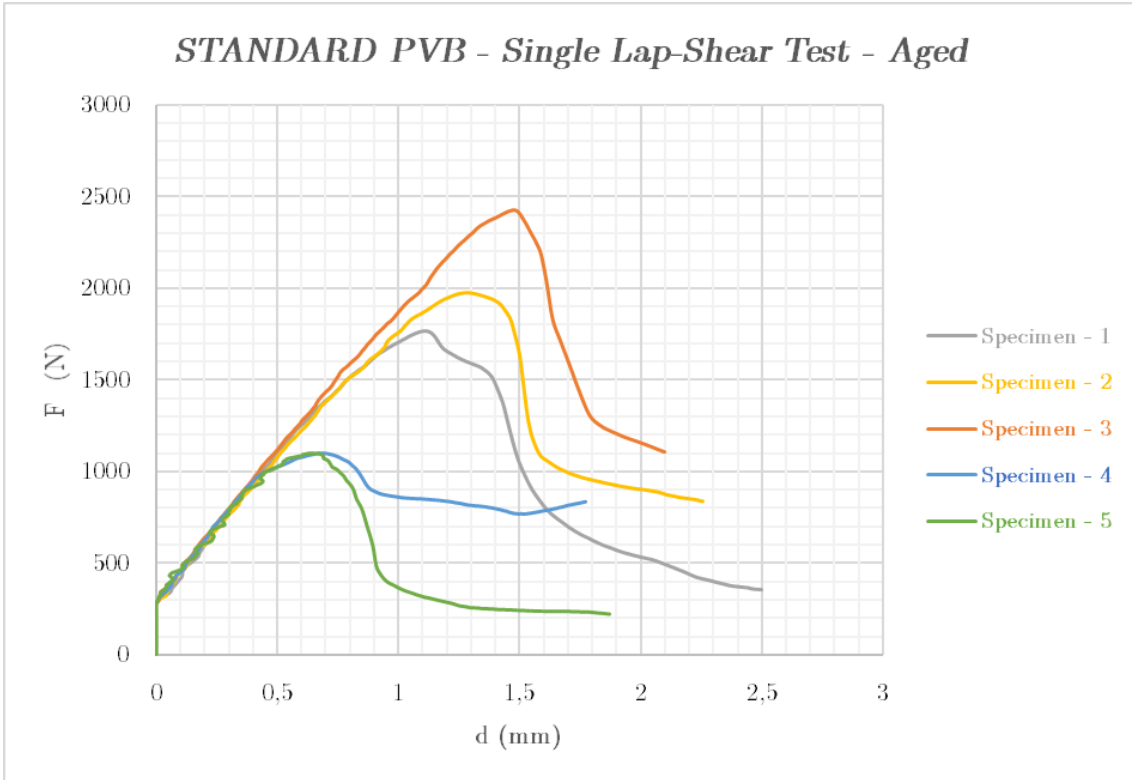


Figure 4.25 Load-displacement diagram of aged standard PVB

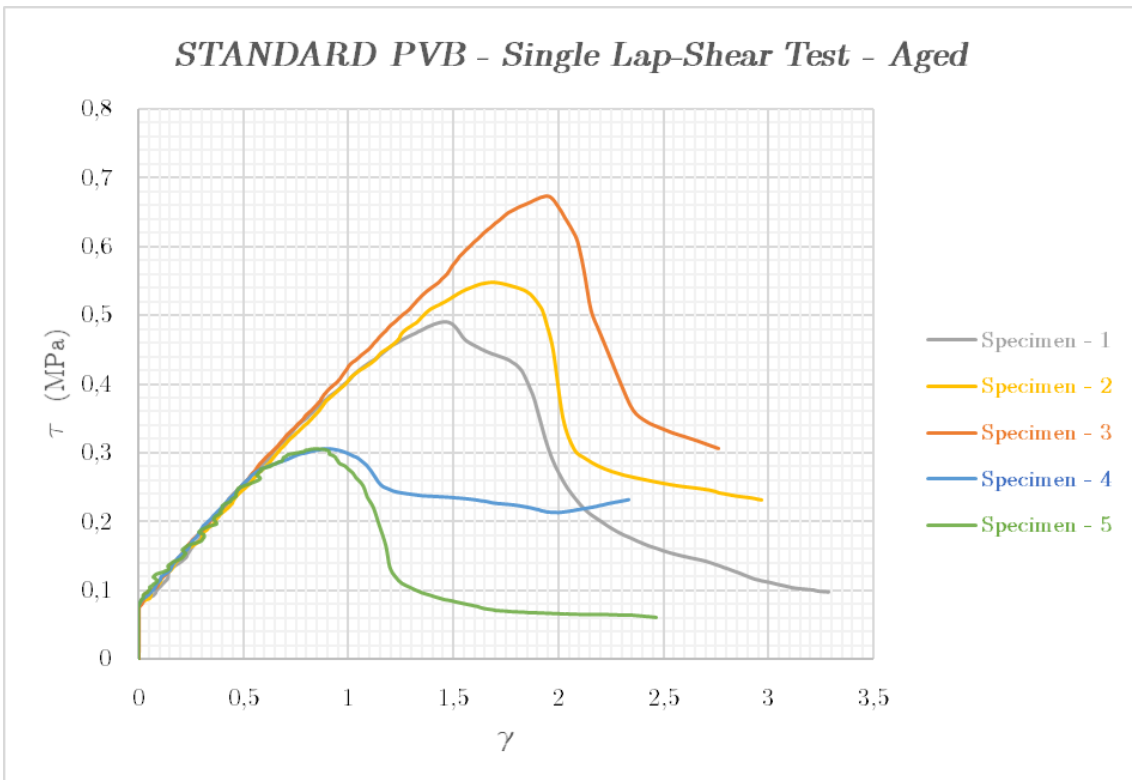


Figure 4.26 Stress-strain diagram of aged standard PVB

Table 4.6 Mean value of aged standard PVB single lap-shear test

Standard PVB - Aged				
	F_{\max} (N)	K (N/mm)	τ_{\max} (MPa)	G (MPa)
PVB - 1	1766	1697	0,49	0,36
PVB - 2	1975	1603	0,55	0,34
PVB - 3	2426	1679	0,67	0,35
PVB - 4	1103	1739	0,31	0,37
PVB - 5	1103	1527	0,31	0,32
Average	1675	1649	0,47	0,35
St. dev	574	84	0,16	0,02
σ^*	34,26%	5,12%	34,26%	5,12%

Figure 4.27 shows how, as occurred for the aged tensile tests, humid and hot environment decrease the performance of the laminated glass with standard PVB.

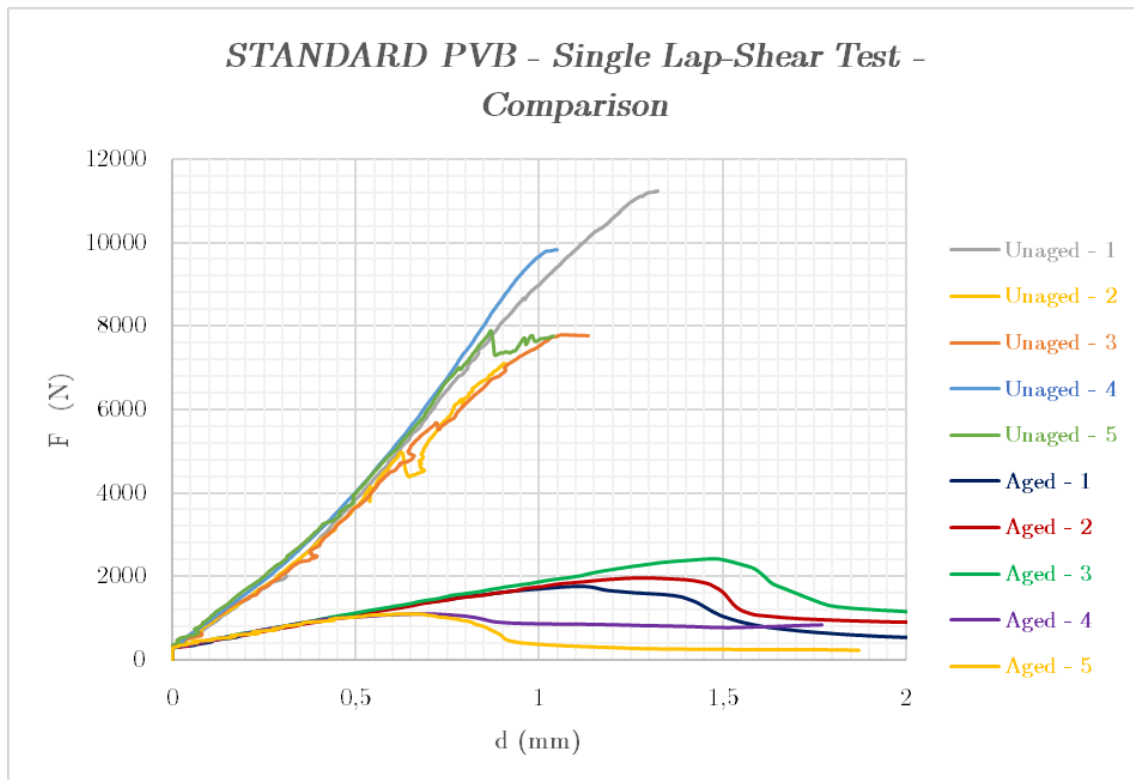


Figure 4.27 Comparison between average load-displacement diagram of unaged and aged standard PVB

After two weeks in a climatic chamber, the aged standard PVB samples show on average a 78.4% reduction in maximum load at failure than the unaged standard PVB ones (respectively, 2.426 kN and 11.232 kN).

As evidenced by this result, the use of laminated glass with PVB in humid and/or hot environments (e.g., swimming pools, showers and greenhouses) is strongly discouraged, as, with the passage of years, the glass panel almost completely loses its mechanical, physical and optical properties (phenomena such as delamination and yellowing of the plastic may occur).

Nano-net PVB

Results were plotted in a load-displacement diagram (Figure 4.28) and in a stress-strain diagram (Figure 4.29). The mean values are presented in Table 4.7.

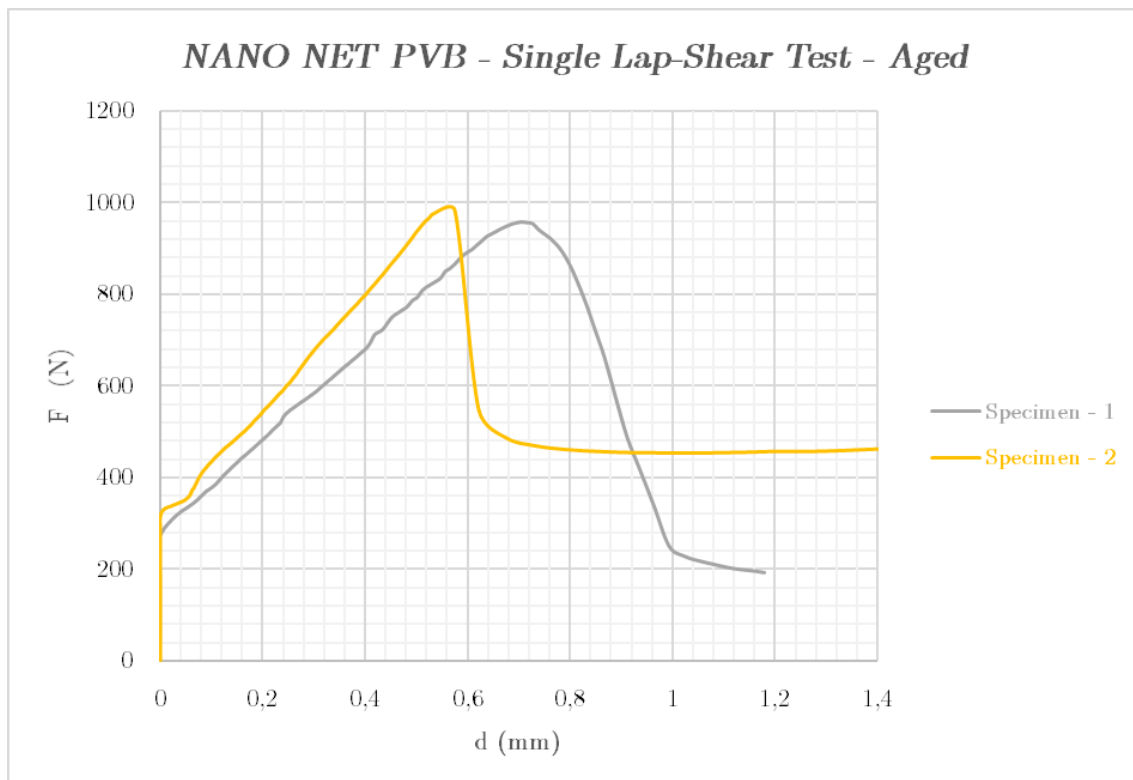


Figure 4.28 Load-displacement diagram of aged nano-net PVB

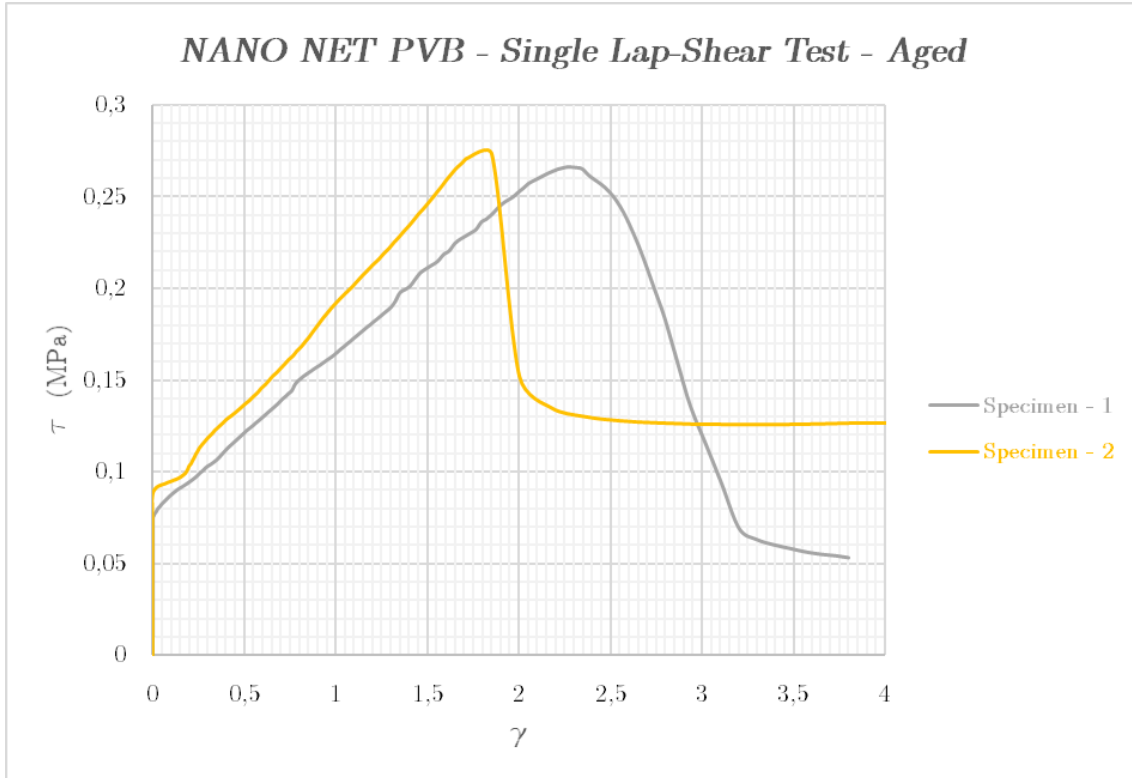


Figure 4.29 Stress-strain diagram of aged nano-net PVB

Table 4.7 Mean value of aged nano-net PVB single lap-shear test

Nano-net PVB - Aged				
	F_{\max} (N)	K (N/mm)	τ_{\max} (MPa)	G (MPa)
PVB - 1	958	1022	0,27	0,09
PVB - 2	983	1188	0,27	0,10
Average	971	1105	0,27	0,10
St. dev	18	117	0,00	0,01
σ^*	1,81%	10,61%	1,81%	10,61%

Figure 4.30 shows the decrease of the performance of the laminated glass with nano-net PVB caused by ageing test.

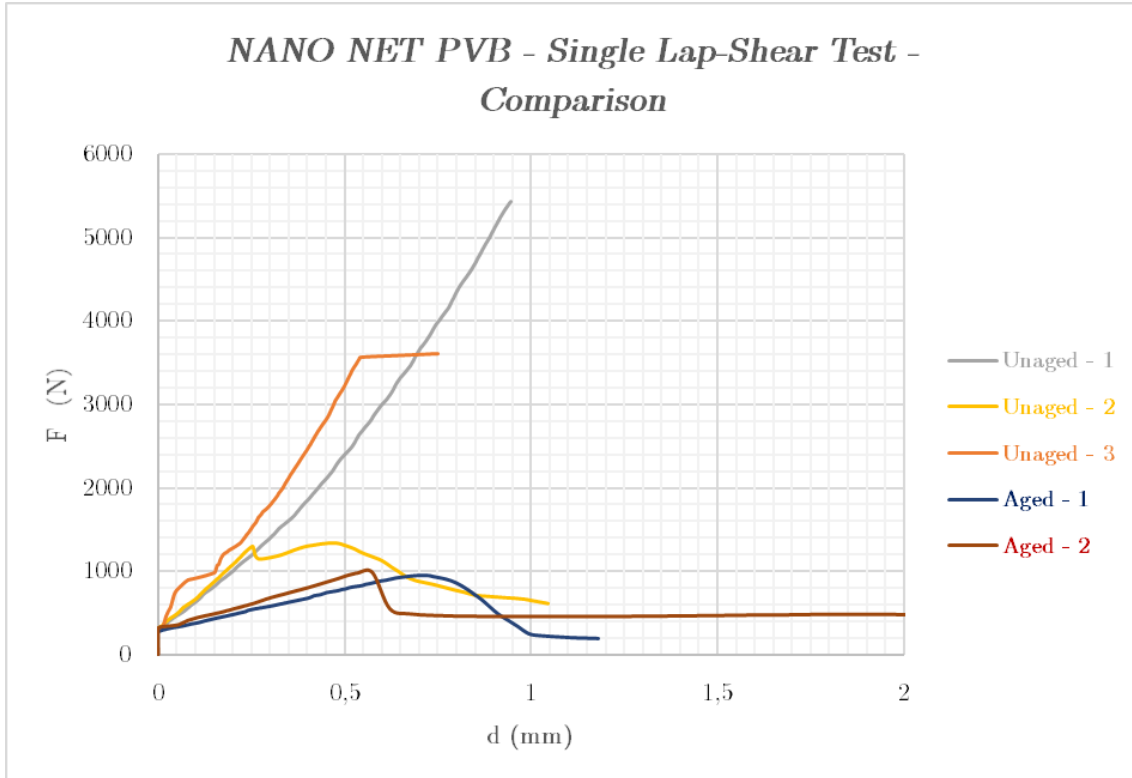


Figure 4.30 Comparison between average load-displacement diagram of unaged and aged nano-net PVB

While aged standard PVB showed a 78.4% maximum breaking strength reduction, nano-net PVB undergoes an 81.9% reduction compared to unaged specimens (5.433 kN before ageing and 0.983 kN after ageing). This higher reduction in performance is due to the greater porosity of the nano-net PVB which is able to absorb more water and consequently leads to a greater reduction in the maximum achievable load.

4.6 UV-Vis Test

The data processing on the optical and energy performance allowed calculating the light, solar and ultraviolet transmittance values on small areas of each specimen (standard PVB and nano-net PVB). For these samples spectrophotometric tests were carried out on the central portion and the main values reported in the relative graphs. The following parameters were calculated:

- The light transmittance τ_v is the transmittance property in the visible range, calculated as the fraction of the incident light that is transmitted by the laminated glass. It was calculated using the following formula (according to UNI EN 410:2011 [22]):

$$\tau_v = \frac{\sum_{\lambda=380 \text{ nm}}^{780 \text{ nm}} D_\lambda \tau(\lambda) V(\lambda) \Delta\lambda}{\sum_{\lambda=380 \text{ nm}}^{780 \text{ nm}} D_\lambda V(\lambda) \Delta\lambda}$$

Where:

- D_λ is the relative spectral distribution of illuminant D65 [K];
- $\tau(\lambda)$ is the spectral transmittance [%] of the laminated glass experimentally determined;
- $V(\lambda)$ is the spectral luminous efficiency for photopic vision [lm/W] defining the standard observer for photometry;
- $\Delta\lambda$ is the wavelength interval [nm].

The values for $D_\lambda V(\lambda) \Delta\lambda$ were obtained from Table 1 of the standard [22]. A higher light transmittance value means that there is more daylight in a space with a consequent reduction of electric lighting consumptions.

- The solar transmittance τ_e is the fraction of incident solar radiation that is directly transmitted by the laminated glass. It was calculated using the following formula (according to UNI EN 410:2011 [22]):

$$\tau_e = \frac{\sum_{\lambda=300 \text{ nm}}^{2500 \text{ nm}} S_\lambda \tau(\lambda) \Delta\lambda}{\sum_{\lambda=300 \text{ nm}}^{2500 \text{ nm}} S_\lambda \Delta\lambda}$$

Where:

- S_λ is the relative spectral distribution of the solar radiation [W/m^2];
- $\tau(\lambda)$ is the spectral transmittance [%] of the laminated glass experimentally determined;
- $\Delta\lambda$ is the wavelength interval [nm].

The values for $S_\lambda \Delta\lambda$ were obtained from Table 2 of the standard [22].

- The UV transmittance τ_{uv} is the percentage of incident ultraviolet energy that is directly transmitted through the laminated glass. It was calculated using the following formula (according to UNI EN 410:2011 [22]):

$$\tau_{uv} = \frac{\sum_{\lambda=280 \text{ nm}}^{380 \text{ nm}} U_\lambda \tau(\lambda) \Delta\lambda}{\sum_{\lambda=280 \text{ nm}}^{380 \text{ nm}} U_\lambda \Delta\lambda}$$

Where:

- U_λ is the relative spectral distribution of the UV part of global solar radiation [W/m^2];
- $\tau(\lambda)$ is the spectral transmittance [%] of the laminated glass experimentally determined;
- $\Delta\lambda$ is the wavelength interval [nm].

The values for $U_\lambda \Delta\lambda$ were obtained from Table 3 of the standard [22].

Figure 4.31 and Figure 4.32 shows, respectively, the recorded spectrum of standard PVB and the recorded spectrum of nano-net PVB obtained by the UV-Vis tests. A comparison between the material is presented in Table 4.8.

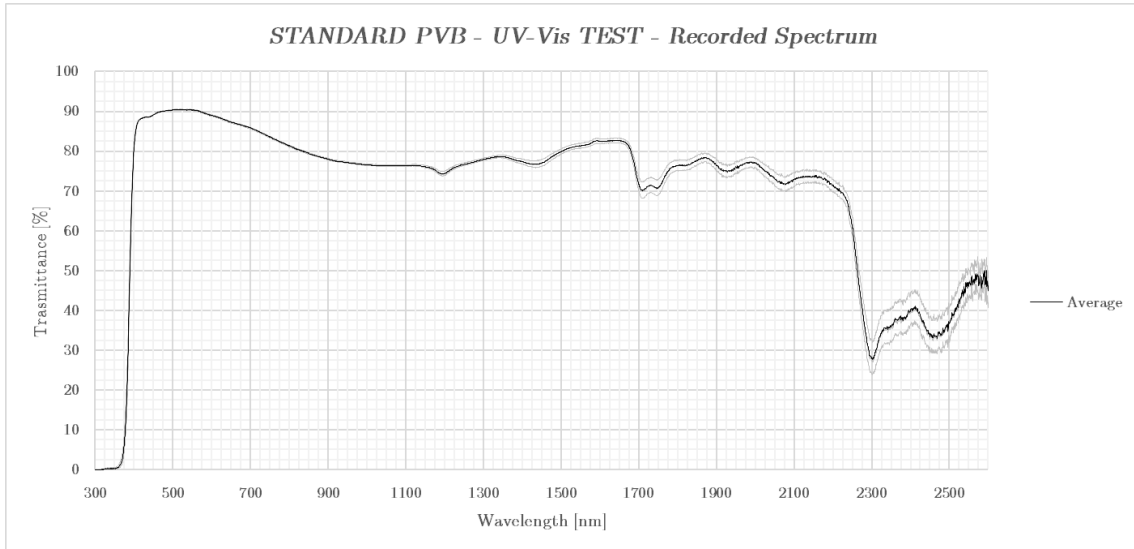


Figure 4.31 Recorded spectrum for standard PVB

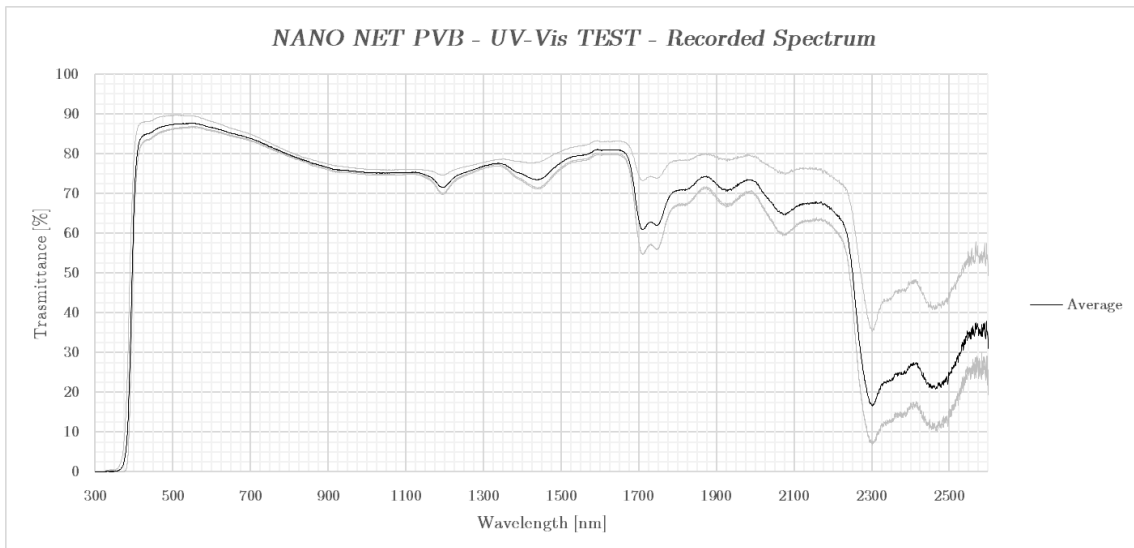


Figure 4.32 Recorded spectrum for nano-net PVB

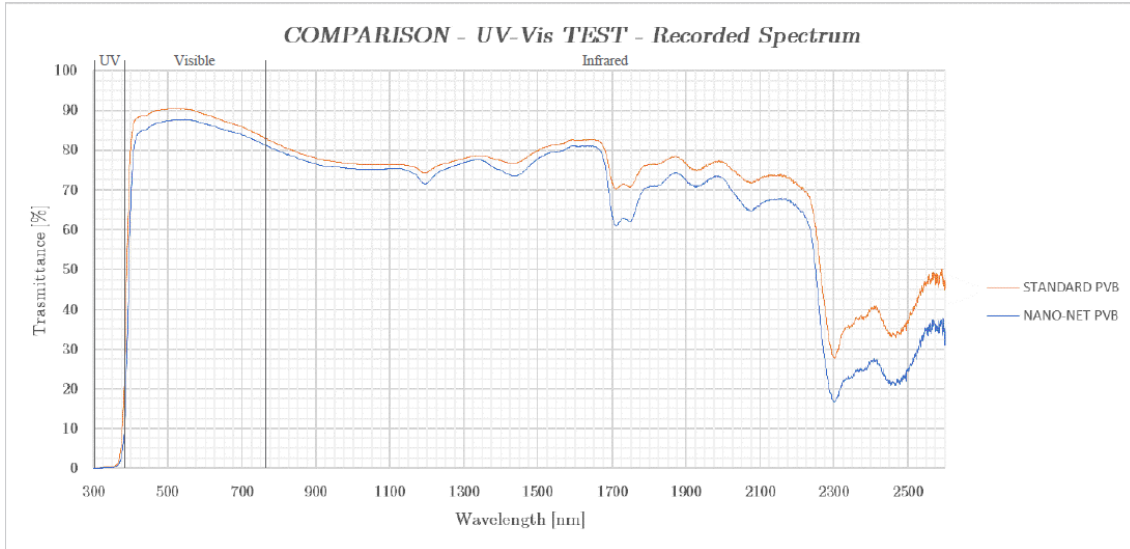


Figure 4.33 Comparison between standard PVB recorded spectrum and nano-net PVB recorded spectrum

As shown in the previous graphs, comparing the recorded spectrum of the standard PVB and the recorded spectrum of the nano-net PVB, it can be seen that the two materials have a behaviour similar to the transmission of electromagnetic radiation.

In the UV region (280 nm ÷ 380 nm), the two materials block more than 98% of the electromagnetic radiation. A UV resistant plastic material will not show changes in appearance such as: yellowing, discoloration and whitening of the surface with formation of stress crack. Furthermore, due to this property, PVB-laminated glasses are used in applications for the protection of works of art from UV rays.

In the visible region (380 nm ÷ 760 nm), standard PVB revealed little better properties, with the highest value of light transmittance.

In the near-infrared and in the first part of the medium-infrared (760 nm ÷ 2500 nm), instead, the transmittance values for nano-net PVB are slightly less than standard PVB. This allows to have a better behaviour and to avoid undesired heat gains and winter heat losses.

What has been described so far is confirmed by the values calculated according to UNI EN 410:2011 [22] and shown in the Table 4.8. To summarize, the standard PVB shows a better light transmission while the nano-net PVB has a better behaviour both in the UV range and in the infrared range.

Table 4.8 Mean values of light, solar and UV transmittance for standard PVB and nano-net PVB

Parameters	Standard PVB	Nano-net PVB
Light transmittance τ_v	89.79%	87.11%
Solar transmittance τ_e	78.71%	76.26%
UV transmittance τ_{uv}	2.04%	0.91%

Chapter 5

Conclusions and Future Work

5.1 Conclusions

The main aim of the work was to evaluate if other PVB shapes than continuous film, for example nano-net, could lead to better mechanical or thermo-physical properties for this material. Indeed, this improvement was demonstrated in literature for other types of supports (for example laminated phenolic composites).

Several mechanical and thermo-physical experimental tests allowed demonstrating that the nano-net brings improvements compared to the standard PVB only on energy aspects while determines some drawbacks as regard mechanical issues. Indeed, it determines:

- Greater water absorption, which could lead to delamination phenomena of the laminated glass;
- A reduction in elongation and in the relative ultimate tensile strength at failure but with an increase in the toughness of the material (three fundamental parameters that influence the global behavior of laminated glass);
- A reduction in the adhesion capacity between glass and plastic interlayer with consequent loss of performance of the structure;
- Slight loss in visible light transmittance, but a significant improvement in the solar radiation range.

5.2 Future Work

Future works could be focused on the improvement of the still open issue of scarce mechanical behavior of PVB nano-net. Indeed, since outstanding mechanical performance were obtained by nanowebs in the field of laminated phenolic with resins, some applications could envisage the adoption of structural adhesives or suited resins to improve the adhesion between plastic interlayer and glass. Such resins could also hinder the problem of increased water uptake.

Moreover, remaining in the field of nano-networks, further surveys could analyze the performance of PVB nano-net with different thicknesses or with different amounts of plasticizer and their interactions with glass.

Bibliography

- [1] Camilla Fors. *Mechanical Properties of Interlayers in Laminated Glass, Experimental and Numerical Evaluation*. Department of Construction Sciences, LUND University, 2014.
- [2] Glasforskningsinstitutet Glafo. *Boken om glas*. Glafo, Växjö, 2nd edition edition, 2005.
- [3] Eric Le Bourhis. *Glass; Mechanics and Technology*. WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, 2008.
- [4] Pilkington. *The float process*. <http://www.pilkington.com/pilkingtoninformation/about+pilkington/education/float+process/default.htm>.
- [5] Michael Patterson. *Structural Glass Facades and Enclosures*. John Wiley & Sons, Inc., Hoboken, New Jersey, 2011.
- [6] Matthias Haldimann, Andreas Luble, and Mauro Overend. *Structural Use of Glass*. ETH Zürich and International Association for Bridge and Structural Engineering, Zürich, 2008.
- [7] Carlson Per-Olof. *Bygga med glas*. Ljungbergs Tryckeri AB, 2005.
- [8] Albrecht Schutte and Werner Hanenkamp. *Zum Tragverhalten von Verbund- und Verbundsicherheitsglas bei erhöhten Temperaturen unter Einwirkung von statischen und dynamischen Lasten*. volume 76. Bautechnik, 1999.

- [9] COST. *COST Action TY0905 Mid-term Conference on Structural Glass*. CRC Press, Leiden, The Netherlands, 2013.
- [10] Marc Martin, Xavier Centelles, Aran Solé, Camila Barreneche, A. Inés Fernández, Luisa F. Cabeza. *Polymeric interlayer for laminated glass: A review*. Construction and Building Materials, ScienceDirect, 2019.
- [11] Maria Fröling. *Strength Design Methods for Glass Structures*. Lund University, 2013.
- [12] J.A. Hooper. *On the Bending on Architectural Laminated Glass*. International Journal of Mechanical Sciences, Pergamon Press, 1972.
- [13] R.A. Behr, J.E. Minor, M.P. Linden, and C.V.G Vallabhan. *Laminated Glass Units Under Uniform Lateral Pressure*. Journal of Structural Engineering, 1985.
- [14] Hossein Ipakchi, Amir Masoud Rezaoust, Masoud Esfandeh, Mohammad Rezei. *An investigation on the effect of polyvinyl butyral interlayer forms on the fracture toughness of glass reinforced phenolic laminates*. Thin-Walled Structures, ScienceDirect, 2020.
- [15] UNI EN ISO 11357-1. *Materie plastiche – Calorimetria differenziale a scansione (DSC) – Parte 1: Principi generali*. Novembre 2016.
- [16] UNI EN ISO 11357-2. *Materie plastiche – Calorimetria differenziale a scansione (DSC) – Parte 2: Determinazione della temperatura di transizione vetrosa e dell'altezza del gradino*. Luglio 2020.
- [17] UNI EN ISO 62. *Materie plastiche – Determinazione dell'assorbimento d'acqua*. Agosto 2008.
- [18] UNI EN ISO 527-1. *Materie plastiche – Determinazione delle caratteristiche a trazione – Parte 1: Principi generali*. Novembre 2019.

- [19] UNI EN ISO 527-3. *Materie plastiche – Determinazione delle caratteristiche a trazione – Parte 3: Condizioni di prova per film e lastre*. Febbraio 2019.
- [20] UNI EN 1465. *Adesivi – Determinazione della resistenza al taglio per trazione di assemblaggi a substrati incollati*. Aprile 2009.
- [21] UNI EN ISO 12543-4. *Vetro per edilizia – Vetro stratificato e vetro stratificato di sicurezza – Parte 4: Metodi di prova per la durabilità*. Dicembre 2011.
- [22] UNI EN 410. *Vetro per edilizia – Determinazione delle caratteristiche luminose e solari delle vetrate*. Marzo 2011
- [23] Xavier Centelles, Marc Martìn, Aran Solé, J. Ramon Castro, Luisa F. Cabeza. *Tensile test on interlayer materials for laminated glass under diverse ageing condition and strain rates*. Construction and Building Materials, ScienceDirect, 2020.
- [24] Emanuela Speranzini, Stefano Agnetti, Marco Corradini. *Experimental analysis of adhesion phenomena in fibre-reinforced glass structures*. Composites Part B, ScienceDirect, 2016.
- [25] Xavier Centelles, J. Ramon Castro, Luisa F. Cabeza. *Double-lap shear test on laminated glass specimens under diverse ageing conditions*. Construction and Buildings Materials, 2020.
- [26] Wikipedia. *Electrospinning*.
<https://en.wikipedia.org/wiki/Electrospinning>
- [27] Francesca Stazi, Margherita Giampaoli, Francesca Tittarelli, Costanzo di Perna, Placido Munafò. *Durability of different glass coating in humid and saline environments, ageing impact on heat light transmission and thermal comfort*.
- [28] Wikipedia. *Spectrophotometry*.
<https://en.wikipedia.org/wiki/Spectrophotometry>