Polymeric interlayer materials for laminated glass: A review

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Abstract

Laminated glass is obtained by bonding two or more glass layers using a polymeric interlayer. Compared to monolithic glass, laminated glass is beneficial in terms of post-breakage safety, security against break-ins, and acoustic insulation, among others. That is why laminated glass is being used for a wide variety of constructive solutions. Polymers such as PVB, ionomers, EVA and TPU are used as interlayer materials in laminated glass. This review aims to describe the most common polymeric interlayers, outline its characterization techniques, and give a general overview about the recyclability of the interlayers. There are two main properties used to characterize the interlayer materials: mechanical properties and resistance to ageing factors. Main mechanical tests found in the literature are summarized, and the properties studied in each of them are listed. Most experimental studies regarding ageing resistance consider mainly three weathering agents: humidity, UV radiation, and temperature.

Keywords: Interlayer; Polymer; Laminated glass; Ageing resistance; Mechanical properties; Recyclability

Nomenclature:

ATR: Attenuated total reflectance

CDM: Continuum damage mechanics

CIP: Cast in place

CST: Compressive shear test

CZM: Cohesive zone models

DMA: Dynamic mechanical analysis

DBS: Dibutyl sebacate

DEM: Discrete element method

DIC: Digital image correlation

DSC: Differential scanning calorimetry

EDM: Element deletion method

EVA: Ethylene vinyl acetate

FEM: Finite element method

FTIR: Fourier transform infrared spectroscopy

GC-MS: Gas chromatography–mass spectrometry

NMR: Nuclear magnetic resonance

PC: Polycarbonate

PET: Polyethylene terephthalate

PMMA: Poly (methyl methacrylate)

PSD: Particle size distribution

PV: Photovoltaic

PVB: Polyvinil butyral

RH: Relative humidity

SEM: Scanning electron microscope

SG/SGP: SentryGlas/SentryGlasPlus

SRP: Steel reinforced polymers

TEM: Transmission electron microscopy

TG/TGA: Thermogravimetric analysis

TPU: Thermoplastic polyurethane

TST: Traction shear test

TTS: Time-Temperature Superposition

UV: Ultraviolet

WLF: William-Landel-Ferry

XFEM: Extended finite element method

1. Introduction

The most common type of glasses for architectural applications, and historically the oldest type of glasses, are silicate glasses based on SiO_2 sand. There is archaeological evidence of the production of glass since approximately 3400 years ago [1,2]. This unique material has been used in construction for 2000 years [3]. In recent decades, its development has been especially notorious in the construction sector, but it is also present in many other fields. These fields include, but are not limited to, transport and energy. In the automotive industry, for instance, glass contributes to 2.6% to the total weight of North American light vehicles [4] and in the energy sector it is used to encapsulate photovoltaic (PV) modules. In addition, demand tends to increase according to industry market studies: the global demand for flat glass is forecast to advance 6.6% per annum (Figure 1) [5].

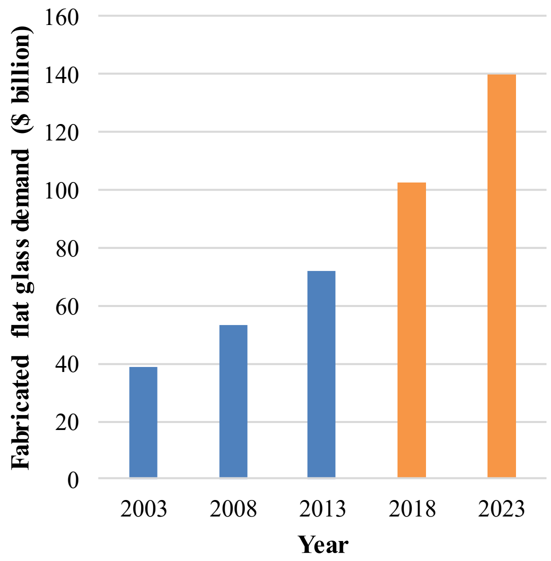

Figure 1. Word flat glass demand forecast, adapted from [5].

Approximately 1500 million tonnes of materials were consumed per annum in the building sector in Europe between 2003 and 2011. Flat glass represented 0.4% (5.5 million tonnes) of that total weight. A big portion (65.5%) of the total flat glass production was used in the building sector [6] The portion used in the building sector will tend to increase taking into account that the application of glass as a construction material increased in the last years [7]. This interest can be easily explained considering glass unique characteristics, such as high transparency, resistance to corrosion, and recyclability, as well as good mechanical properties and a relatively low energy demand for its production [7].

Nevertheless, glass presents some limitations, especially in terms of safety, for some of its applications. Monolithic glass is a brittle material, without capacity to deform plastically or absorb energy in case of impact [9]. Because of that, failure of glass generally occurs when tensile stresses are applied on small surface flaws [10,11] that may appear during the manufacturing, transportation, assembly, or service life of glass [12-14]. When the applied stress exceeds a certain value, which will depend on the crack shape and size, it can lead to crack growth and therefore glass breakage. These surface micro-defects depend on both the particular type of glass and the procedure followed during its preparation, and can be considered disturbing elements of stress [15]. In the thirties, the automotive industry conceived laminated glass in order to reduce the risk and the severity of injuries caused by glass breakage on both users of the vehicle and pedestrians [16,17].

There are reviews that provide information about laminated glass panels, especially for failure analysis in automotive applications [17-19] and for structural applications [20,21]. However, these review articles do not focus on the mechanical and physical properties of the interlayer alone. There is also a review on interlayer materials for laminated glass [22], which studies laminated glass made with different types of interlayers: UV curable resin, casted film, and a combination of both. This review article focuses on the synthesis, properties, and applications of PVB, polycarbonates, and polyurethane based interlayers.

The main goal of this review is to provide information about the most commonly used interlayer materials for laminated glass: polyvinyl butyral (PVB), ethylene-vinyl acetate (EVA), ionomers, and thermoplastic polyurethane (TPU). The best interlayer candidate may be different for each application, depending on the most relevant requirements. In addition to that, it may be useful to anticipate which is the most suitable interlayer before performing the bonding process to obtain laminated glass; that is why the review includes a comparison between the performance of the interlayer alone and the interlayer in laminated glass.

2. Laminated glass

Laminated glass is a glass unit that consists of at least two glass panels and one intermediate polymeric layer (interlayer), whereby the glass panels are bonded to the interlayer in the manufacturing process [23]. The bond occurs due to the chemical union between hydroxyl groups (polymer) and silanol groups (glass) [24]. This type of chemical bond happens for all interlayers with hydroxyl groups, which most of them have, including PVB, TPU, EVA, and ionomers. This composite material greatly improves the behaviour of glass, both before and after breakage. Before breakage, when a laminated glass panel is subjected to out-of-plane bending, the interlayer material transfers shear stresses between confronted glass surfaces, and as a consequence it affects its bending stiffness: the stiffer the interlayer, the higher the out-of-plane bending stiffness of laminated glass panels. [25]. In the case of glass breakage, the broken glass shards remain attached to the interlayer. In some cases, depending on the loading scenario and interlayer stiffness, the interlayer can bridge cracks by the adjacent unbroken panels [8,26,27]. Applied forces that make cracks appear and propagate can be redirected by shear stresses into the interlayer material to the adjacent unbroken glass layers; that crack blocking mechanism prevents cracks from opening up over the laminate [28]. On account of these bonding properties, laminated glass presents a certain level of residual strength after breakage [9]. That is because the interlayer material can provide a certain level of tensile stress, while the broken glass shards can still provide compressive strength, but not tensile. Consequently, laminated glass has a higher level of post-breakage strength than monolithic glass. The post-breakage strength of laminated glass depends, among other factors, on the interlayer material strength, stiffness, thickness and adhesion level with glass [29].

Interlayer material behaviour has a great influence on the performance of laminated glass elements; its shear stiffness [29,30] and adhesion with glass [31] are of vital importance to the mechanical overall performance of laminated glass. On account of that, laminated glass and interlayer materials have attracted a lot of interest lately. Theoretical study [32], numerical simulation [33-41], and experimental research [42-44] are three ways to investigate the behaviour of interlayer materials, and hence laminated glass.

Since the desired interlayer material properties of laminated glass are transparency and capacity to bond glass sheets, amorphous polymers are the most suitable option. Polymeric interlayer materials can be divided in two main groups depending on the manufacturing process. The first one includes the most common interlayer materials, bonded by means of lamination process: sheet type polymers, such as poylvinil butyral (PVB), ethylene-vinyl acetate (EVA), ionomers (e.g. SentryGlas), thermoplastic polyurethane (TPU), polycarbonates (PC), and polyethylene terephthalate (PET). The second group gathers the cast in place (CIP) interlayers based on polyurethanes (PU), polymethylmehacrylates (PMMA) and epoxies [45]. Even though different polymeric materials have been used as interlayers in laminated glass, it is important to emphasize that until now PVB presents a widespread use in all the fields of application of laminated glass [46,47].

After the implementation of laminated glass in car windshields, the performance and safety improvements provided by the interlayer material allowed its use in several other applications (Figure 2). The contemporary architecture trend is to include glass not only in windows and doors but also in a wide variety of constructive solutions, such as beams, floors or staircases. The possibility of overlapping several glass panels, alternated with polymeric interlayers, and even adding layers of stiff transparent polymers (such as PC or PMMA), can make it more difficult to break and penetrate them. For that reason, laminated glass is also used in security applications such as showcases and bulletproof glass [48-50].

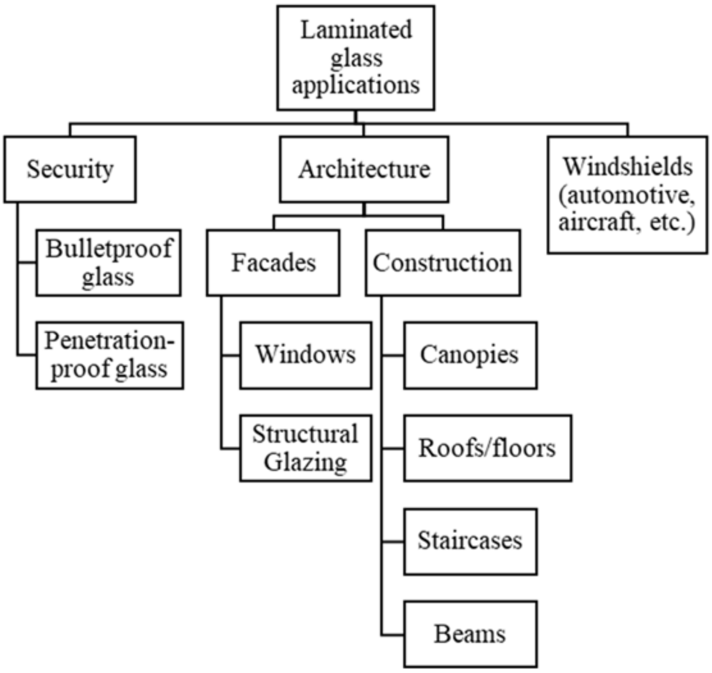

Figure 2. Applications of laminated glass.

Glass failure is not desirable, but it may happen due to unconsidered loads or accidental impacts, among other reasons. Given the brittle behaviour of glass, failure analysis of glass is especially important. Chen et al. [17] studied glass failure due to impact, identifying different methods to predict laminated glass mechanical behaviour. According these authors, six numerical methods have been used to predict glass-ply cracking. The cohesive zone model is one of the most popular algorithms for failure analysis. Other relevant methods used in this field are: discrete element method (DEM), element deletion method (EDM), mainly used in automotive windshield glazing, continuum damage mechanics (CDM), extended finite element method (XFEM), and the combination of finite element method (FEM) with DEM to describe the large deformation behaviour of polymeric interlayers. Several researchers have performed parametric numerical simulations and pointed out that PVB had relevant effects on impact failure [33,34]. Furthermore, numerical methods have been used to model and understand PVB adhesion with glass.

Three types of approaches for the modelling of the bond between glass and PVB (Figure 3) have been reported in the literature. The penalty-based approach [36,37] allows to decompose the calculation domain into discrete element areas and finite element areas to calculate the relative displacements between glass and PVB by adding penalty springs. In the shared-node method the glass and the PVB is connected via a tied contact algorithm, a constraint-based contact method where tied contact elements are automatically deleted along with the failure of all connected glass nodes [38]. Recently, intrinsic cohesive zone models (CZM) seem to be suitable to model the imperfect bonding between glass and PVB [35] and model delamination phenomena in various composite materials [39-41].

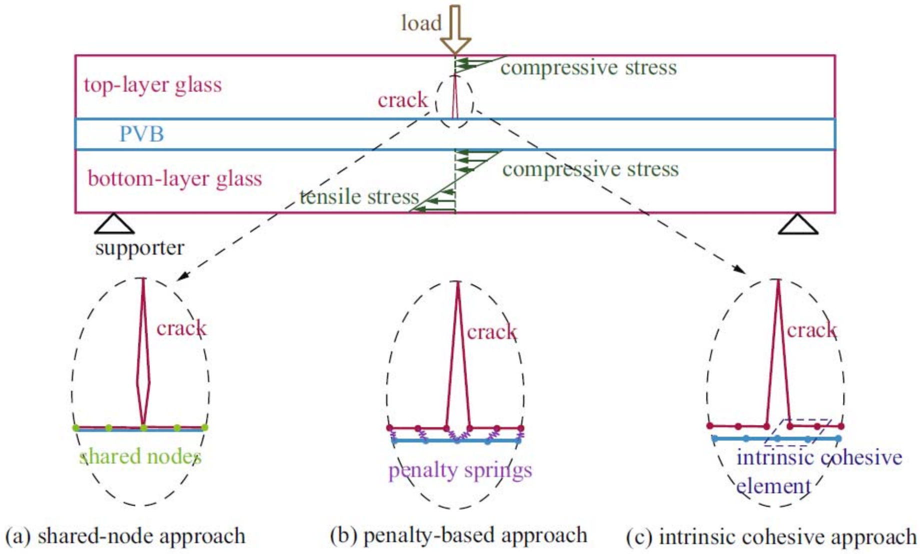

Figure 3. Numerical approaches for the modelling of the adhesion glass-PVB in cracked laminated glass [17].

For the numerical analysis of laminated glass and interlayer material in particular, elastic, hyperelastic, plastic, and viscoelastic models have been adopted for the deformation modelling [17]. Interlayer materials for laminated glass have been extensively characterized in experimental studies, mainly regarding ageing resistance [28,29,44,51-56], mechanical properties [57-62] and recyclability [63-66]. The action of weather: moisture, temperature cycles, and solar radiation have been identified as key factors on physical and mechanical properties during the lifetime of the interlayer materials. For instance, in a PV cell, weathering conditions may decrease strength of the encapsulation material (typically EVA) reducing PV module lifetime by enabling widespread corrosion of internal components [56].

The mechanical response of structural laminated glass elements has to be experimentally evaluated [8,15,28]. This can be achieved through digital image correlation (DIC) technique [15]. In order to design laminated glass with structural function, the thermo-viscoelastic response of the polymers used as interlayer materials have to be considered and characterized [42,43].

Although the structural use of lass in buildings is increasing, there is no Eurocode for structural glass yet. However, there is a European pre-normative document that collects information from national codes and establishes the procedure that should result in a new Eurocode of structural glass [68]. In Europe, there are many national standards for the design and construction of glass elements in buildings, such as the ones from Germany [69], Austria [70], Czech Republic [71], Netherlands [72,73], United Kingdom [74,75,76], France [77], and Italy [78,79].

Worldwide, automotive industry produces annually more than 90 million of vehicles [81] that use laminated glass in windshields for safety purposes. Therefore, from the environmental perspective, another factor that must be considered is the recyclability. From this point of view, interlayer material recycling should be addressed in a sustainable and environmentally friendly route [64,65]. While glass is commonly recycled, interlayer materials are not. Interlayer materials end as disposable by-products of the glass recycling industry. A common alternative to the disposal in a landfill is to recycle them by mechanical processes or valorise them in other applications [82]. However, recycled PVB presents variations in its structure and lower properties than the original polymer [63]. In order to quantify this degradation, several authors characterized raw and recycled PVB from the automotive industry [63,65]. New recycling and separation methods were also studied such as the mechanochemical separation method proposed by Swain et al. [65]. Moreover, Burmistrov et al. [66] investigated the possibility of secondary PVB recycling as composite coatings with high mechanical properties.

Ranocchiai et al. [67] reviewed the experimental tests carried out to determine the dynamic properties of the interlayer materials in laminated glass. The study included static monotonic tests, dynamic tests, and creep or relaxation tests, for interlayer materials, either out of laminated glass or in laminated glass. These authors highlighted the limitations of static monotonic tests to characterize viscoelastic materials. Dynamic and creep or relaxation tests are needed to accurately describe the short- and long- term behaviour of these materials. For the characterization of interlayer materials, Ranocchiai et al. recommended using an effective elastic modulus that depends on both the load duration and the temperature.

Teotia et al. [18] in 2012 listed the synthesis methods, applications and properties of three interlayer materials (PVB, PC, TPU), and described the different types of laminated glass and lamination methods based on the interlayer material. The aim of this review is to do a state of the art of the available published studies associated with the interlayer materials with a special emphasis in characterization methods, ageing tests and recycling processes. This review deals specifically with the different techniques and methodologies used to characterize the key properties of interlayer materials. The authors describe utilised methodologies and establish a common pattern in the characterization techniques upon interlayer materials. In order to achieve this goal, first, main interlayer materials (PVB, SentryGlas, EVA, and TPU) are described. Afterwards, characterization techniques found in the literature are categorised based on analysed attributes. Ageing resistance, mechanical properties and recyclability are considered as key attributes. Numerical simulation studies concerning laminated glass are out of the scope of this review, but necessary to do a step forward in laminated glass research and will be considered for further work.

3. Interlayer materials

Several types of polymers are used as interlayer for laminated glass; these polymers are amorphous and, usually, weakly cross-linked. While crystalline polymers are usually opaque because of light scattering on the numerous boundaries between phases, amorphous polymers exhibit a certain degree of transparency [83]. Amorphous polymers are characterized by a slow transition from liquid to solid state, passing through viscous behaviour, without latent heat of phase transition. Viscoelastic behaviour, which heavily depends on temperature, is typical of a specific temperature range that is called rubberlike domain. Usually in laminated glass, the interlayer exhibits rubberlike behaviour at room temperature. For this reason, in case of glass breakage, it can produce a bridge ligament among glass fragments. In fact, glass fracture is not able to propagate within soft polymer interlayer but deviates at the interface between glass and interlayer. The main interlayer materials (PVB, ionomer, EVA, and TPU) commonly used for laminated glass are first described in this section.

3.1. PVB - Polyvinyl butyral, Poly [(2-propyl-1,3-dioxane-4,6-diyl)methylene]

PVB was the first material used as interlayer for laminated glass in the thirties. It is formed from the reaction of polyvinyl alcohol with butyraldehyde. The chemical structure used in commercial PVB interlayers is the same for every manufacturer (Figure 4). PVB can be defined as an amorphous random terpolymer and it is composed of three different monomers providing specific properties [84,85]:

- 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.

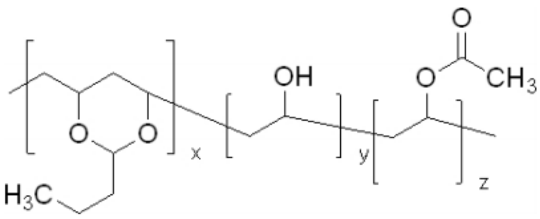

Figure 4. PVB chain structure [64].

Even though the chain structure is the same, the specific properties of each PVB sheet depend on the PVB type, manufacturer, and PVB sheet composition. PVB chains with higher molecular weight provide toughness to the interlayer; therefore, plasticizers must be incorporated in order to improve the material elasticity. This interlayer is mostly used in the form of plasticized. Dhaliwal et al. [63] studied commercial PVB determining that it contains between 20% and 25% of plasticizer and dibutyl sebacate (DBS) was identified as the dominant. Other plasticizers used are triethylenglycol-di-2-ethylbutyrate, tetraethylenglycol-di-heptanoate, butyl phenyl phthalate, triethylene glycol di-(2-ethylhexanoate), and dihexyl adipate [85]. Certainly, the plasticizer must not affect adhesion to glass, migrate out of polymer matrix during processing, nor affect optical properties (i.e. generate haze or yellowness) [34].

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 hydrolysed which leads to the formation of poly(vinylalcohol). In the last step it reacts with butyraldehyde to form butyral cyclic compounds. There is a direct relationship between the mechanical behaviour of PVB and its chemical structure, and therefore, its performance. PVB chemical structure mainly depends on the conditions of the synthesis process. Nevertheless, all PVB commercial available products present similar structure, for instance, Elziere et al. [85] found an average molecular weight of 197 kg/mol with a polydispersity of 1.42 in commercial PVB by means of size extrusion chromatography.

This polymer provides excellent optical and mechanical properties to laminated glass, high mechanical strength, high deformation before breakage, good adhesion to glass (after laminating process), and high light transmission [86]. 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 [51]. Table 1 shows the properties of the PVB sheets, with 0.76 mm of thickness, from the three main manufacturers [87-89]. 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 plasticiser, which increases its glass transition temperature and therefore its stiffness.

Polymer glass transition temperature (T_g) is typically defined as a temperature range, although in the case of PVB this broad range is caused by the varying plasticizer content, and the test method chosen to determine the T_g (DSC, DMA, Dilatometry, etc.) may also affect the result. There is also the possibility to improve other properties of the PVB, for example, increase its transparency or its acoustic insulation.

Table 1. Commercial PVB main properties (foil thickness 0.76 mm).

Parameter	Value	Units
Standard PVB		
Price	4.02 - 4.82	€/m^2
Density	915 - 1070	kg/m^3
Water absorption (ASTM D-570)	3.6	wt.%
Coefficient of thermal expansion	22-40	$K^{-1} \cdot 10^{-15}$
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	ºC
Joining technique	Lamination, UV curing	-
Structural PVB		
Ultimate tensile strength	33	MPa
Elongation at failure	190	%
Young modulus	2.36	MPa

n.a: stands for not available.

PVB has been the predominant interlayer during more than 70 years. Since its production in 1938 inventive efforts tended toward methods of making the interlayer itself cheaper to produce, easier to handle, less prone to defects during lamination, or improving some of its properties. Due to the maturity of PVB as laminated glass interlayer, several improved PVB products with specific functionalities appeared, such as higher adhesion, acoustic insulation, solar reflectiveness, structural function, security, and decorative purposes. All these improvements allow its application not only in laminated glass for windows and doors but also in PV solar cells, automotive windshields, security glass, and structural glass components.

PVB interlayer for laminated glass is currently manufactured and commercialised by few companies worldwide resulting in a very concentrated and dominated market: Eastman® (EEUU), Kuraray Group (Trosifol® and DuPont®), and Sekisui® (Japan). PVB laminates can be obtained by a conventional lamination process or a UV curing process (resin). Interlayer materials are produced by very few industries, but laminated glass is manufactured by a lot of small industries. The optimal lamination process, which guarantees an adequate adhesion between glass and interlayer, depends on many factors (including interlayer material, number of glass layers, and glass panel size, among others).

An adequate laminating process can have an impact on the overall behaviour of a laminated glass element. The level of adhesion between glass and interlayer may affect the performance of laminated glass in many levels. It may affect the transparency of laminated glass due to the formation of bubbles, its durability, as a result of the penetration of vapour and other elements that might degrade the interlayer, the cohesiveness between layers, and the projection of glass fragments in case of breakage, if these fail to remain bonded to the interlayer.

3.2. Ionomer

In 1964 the term "ionomer" was registered by DuPont® for the first time. Ionomers are a type of ionic polymers which have an ionic content of at most 10 mole% within a non-polar polymer. In general terms, the structure of an ionomer consists of a hydrocarbon backbone containing pendant acid groups which are partially or completely neutralized. These acid groups include carboxylic, sulfonic, thioglycolic, and phosphonic. In the case of the backbone, these include, but are not limited to, polybutadiene, polyestirene, polyethylene, polyoxymethylene, and polypentenamer [90]. The synthesis of ionomers is achieved through copolymerisation of functionalised monomers (acrylic acid, p-styrenesulfonic acid, or methacrylic acid can be used). 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 (Figure 5). Therefore, this material can be classified in the group of thermoplastics [54].

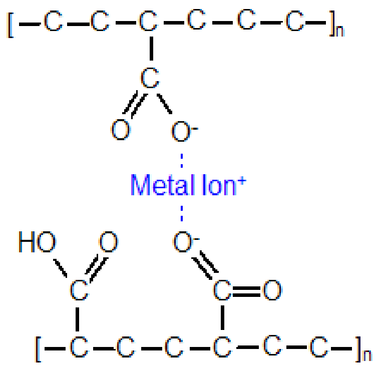

Figure 5. Chemical structure: metal cation bridges two carboxylate anions. Adapted from [55].

Currently, SentryGlas is the only interlayer material for laminated glass based on an ionomer that exists in the market, also called “Ionoplast interlayer”. In this case, ethylene and methacrylic acid copolymer constitute the hydrocarbon backbone of SentryGlas [90].

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. The stiffness value indicated in Table 2 corresponds to a working temperature of approximately 20-25 ºC and a load duration below one hour. Such mechanical properties make SentryGlas a good interlayer for structural laminated glass structures. Furthermore, ionomer interlayer maintains significant advantages over PVB for a large range of temperatures: glass laminated with PVB started to decrease its stiffness at 20 ºC whereas SentryGlas laminates is insensitive to temperature until 55 ºC [90].

Table 2. Commercial SentryGlas main properties (foil thickness 0.76 mm). Values come from technical data sheet provided by the manufacturer.

Parameter	Value	Units
Price	n.a.	€/m^2
Density	950	kg/m^3
Water absorption (ASTM D-570)	n.a.	wt.%
Coefficient of thermal expansion	10 - 15	10^{-5} cm/cm·°C
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 [90]	55	ºC
Joining technique	Lamination	-

*Directly proportional to temperature and time.

3.3. EVA - Ethylene-vinyl acetate, PEVA - Polyethylene-vinyl acetate, VAE - Vinyl acetate-ethylene copolymer

EVA is the copolymer of ethylene and vinyl acetate (VA) (Figure 6), in which the weight percentage of vinyl acetate varies from 10wt.% to 40wt.%, thus belonging to polyolefines. Polymerizing VA with ethylene disturbs the crystal structure and increases the chemical reactivity of the polyethylene (PE).

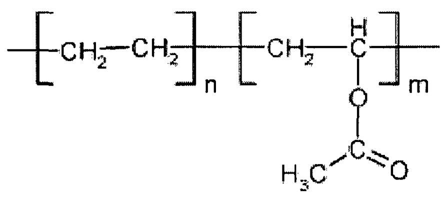

Figure 6. EVA contains ethylene groups (n) and vinyl acetate groups (m).

By varying the VA content in the composition, EVA with significantly different properties are obtained. On that account, three types of EVA copolymer, which differ in the VA content, can be identified (Table 3).

Table 3. EVA behaviour and application depends on VA content.

VA content		Polymer type	Deformation behaviour
Low	up to 4 wt.%	Thermoplastic	Similar to low density polyethylene
Medium	4 to 30 wt.%	Thermoplastic elastomer	It is not vulcanized but presents some of the properties of a rubber (crosslinking)
High	>40 wt.%	Thermoset	Rubber

EVA interlayer material typically contains 32-34wt.% VA and specific additives such as UV absorber, curing agent, photo-antioxidant and thermo-antioxidant [91].

As an interlayer material EVA provides stress-crack resistance, high flexibility, toughness, elasticity and clarity. As shown in Table 4, 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). In most of the cases, due to its chemical structure, EVA is cured in a vacuum lamination oven at 140-155 ºC. 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.

Other available joining techniques are autoclave, with lower pressure and temperature than PVB, or vacuum bag process. On account of these properties and joining techniques alternative to the autoclave, the major application of the EVA interlayer is in PV industry as an encapsulation material.

Nowadays, EVA interlayer for laminated glass is mainly manufactured and commercialised by DuPont® (ELVAX), Bridgestone Corporation (EVASAFE), Evguard, and Argotec (SE-381 and SE-7381).

Table 4. EVA interlayer main properties (foil thickness 0.76 mm).

Parameter	**Value**	**Units**
Price[1]	1.74 - 1.91	€/kg
Density[1]	945 - 955	kg/m^3
Water absorption (ASTM D-570)[1]	0.15 - 0.5	wt.%
Coefficient of thermal expansion [1]	160 - 190	10^{-5} cm/cm·°C
Transmittance[2]	90 - 92	%
Yellowness index[2]	1.9	-
Ultimate tensile strength[1]	9.5 - 10	MPa
Elongation at failure[1]	880 - 930	%
Young modulus[1]	7 - 9	MPa
Poisson's ratio[1]	0.47 - 0.49	-
Glass transition temperature[1]	-77 to -69	ºC
Joining technique	Vacuum lamination, autoclave or vacuum bags	-
Completely crosslinked EVA		
Ultimate tensile strength[2]	20.8	MPa
Elongation at failure[2]	450	%

[1]CES Selector software 2016. Granta Design Limited, Cambridge, UK, 2016, www.grantadesign.com

[2]Commercial EVA technical data sheets

3.4. TPU – Thermoplastic polyurethane

Polyurethane (PU) materials are a wide variety of polymers where all polymer composed of organic units joined by urethane links are included. Although most PU are thermosets, interlayer polyurethanes are composed of thermoplastic polyurethane (TPU), also known as polyurethane elastomer. These polymers are block copolymers with rubbery soft segments and semi-crycaslline or glassy hard segments (Figure 7). On the one hand, soft segments available are of a great extension and will determine properties of the material and its application, for instance, soft segments can be based on polyesters, polycarbonates, polyethers and polycaprolactones. On the other hand, hard segments consist of diisocyanates and short chain diols. Thermoplastic polyurethane can be classified in aliphatic or aromatic TPU, which is dependent upon the isocyanate nature, for instance, toluene diisocyanate, methylene diphenyl diisocyanate and naphthalene diisocyanate lead to aromatic TPU. In contrast, aliphatic isocyanates include for instance hexamethylene diisocyanate, but there is a wide range of aliphatic diisocyanates available which allow for a wide scope of properties. Polyurethane synthesis contains a diverse range of synthetic options, but frequently is selectively produced by a polyaddition reaction from the three basic raw materials: polyol (long-chain diol), short-chain diol, also known as chain extender (G), and diisocyanate (U), in a specially coordinated process. At low temperatures the hard segments are assumed to govern plastic deformation and provide high modulus and tensile strength. On the other hand, at room temperature and above, the soft segments impart the rubber mechanical behaviour.

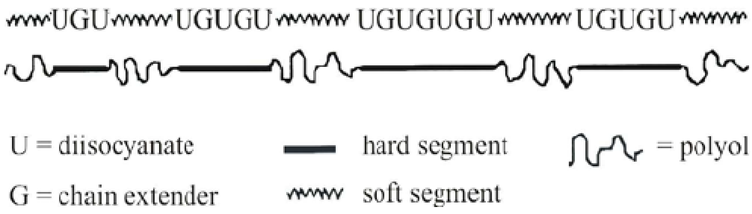

Figure 7. Hard and soft segments of TPU structure [92].

TPU structure depends on diisocyanate, polyol, and chain extender ratio and chemical reaction conditions. The structure ultimately affects the physical and mechanical properties of TPUs. Hydrogen bonds from urethane groups of the hard segments, for example, act as physical crosslinks and are responsible for the elastomeric behaviour of the material.

As an interlayer material, TPU provides a combination of outstanding properties: high tensile strength, toughness, resistance to UV, abrasion and chemical degradation. In fact, TPU bridges the gap between rubbers and plastics [92].

Due to the high bonding strength of TPU with all substrates (glass, PMMA, PC, etc.), it 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.

As interlayer material, TPU presents excellent properties. However, 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. Weller et al. [93] in 2009 combined glass, PC and TPU, creating an innovative hybrid component (Figure 8). Compared to laminated glass beams without PC, this new hybrid beam presented a better post-breakage performance than regular laminated glass beams, thanks to the higher ductility of the PC layer, and was lighter thanks to the lower density of PC compared to glass. In fact, this hybrid component is based on ballistic resistance laminates which combines glass and PC bonded by TPU in a multi-layered laminate. Typically, both the inner and outer layers of the laminates are glass, to provide durability that PC alone cannot provide. The addition of PC layers allows to obtain thicker and lighter panels with a higher capacity to absorb impacts.

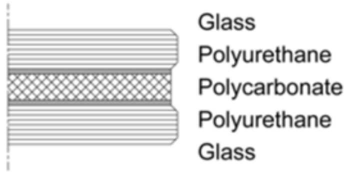

Figure 8. Hybrid beam developed by Weller et al. [93]

During last years, several companies and inventors presented patents in relation to laminated glass with TPU. For instance, Rukavina [94] developed a system with sound attenuation properties. Nowadays, due to the specification of these interlayer applications, only a few companies, such as Huntsman (KRYSTALFLEX®), commercialise TPU sheets.

4. Characterization of interlayer materials

A material characterization of the interlayer materials used for building applications of laminated glass is needed. On account of that, an interlayer material characterization is provided, based on the literature and classified in three main terms: ageing resistance, and mechanical properties.

4.1. Mechanical aspects

4.1.1. Influence of the interlayer

The out-of-plane flexural behaviour of laminated glass is described by Galuppi and Royer-Carfagni [24]. According to these authors, the flexural performance of laminated glass depends on the shear coupling between glass layers through the polymeric interlayer. The mechanical behaviour of laminated glass is located in between the layered limit, when there is no transfer of shear stresses between glass layers, and the monolithic limit, when there is total shear transfer and no relative displacement between confronted glass surfaces. The stronger and stiffer the interlayer, the closer it will be to the monolithic limit. The thickness of the interlayer may also affect its shear stress transfer capacity [113].

Experimental techniques developed to evaluate mechanical response of the interlayer material isolated and in conjunction with glass (laminated glass) are diverse and dissimilar. Table 5 outlines mechanical characterization techniques used in the available literature. In some testing methods on laminated glass specimens, the measured loads and displacements are coupled with the stress and strain of the interlayer. In bending tests, by contrast, the main resistant material is the glass, but the interlayer contributes to the cohesion of the composite laminate. The interlayer material can be subjected to shear stress (bending test, shear strength test, pull-out test), tensile stress (peel test), or a combination of both. The results obtained are described in the following sections.

Table 5. Interlayer mechanical characterization techniques.

Sample	Technique	Output
Interlayer	Uniaxial tensile strength test [58,60-62]	✓ Young's modulus ✓ Poisson's ratio ✓ Yield strength ✓ Strain-hardening characteristics
	Uniaxial compression test [58]	
	Viscosity measurements [57]	✓ Material rheology
	Dynamic mechanical analysis (DMA) [59,108]	✓ Viscoelastic behaviour
Laminated glass	Four-point bending test (EN 1288) [27,28,29,44,57]	✓ Modulus of elasticity in bending ✓ flexural stress and strain
	Pull-out test [28]	✓ Pull out strength ✓ Investigate shear transfer capacity
	Peel test (ISO 8510) [28,**¡Error! No se encuentra el origen de la referencia.**]	✓ Peel strength
	Shear strength measurements: • CST [27,56] • TST [27] • Dynamic torsion test [42,43]	✓ Adhesion properties ✓ Shear stress-strain values

The mechanical behaviour of laminated glass is dependent on the deformability of the interlayer [102], and therefore mechanical analysis cannot be performed without regard to the coupling capability of interlayers. Interlayer materials for laminated glass are subjected to various load conditions, whose duration varies from few seconds (e.g. wind pressure) to several years (e.g. permanent loads), as well as to various thermal conditions. Taking into account the viscoelastic behaviour of interlayer materials, its performance strongly depends on both load duration and temperature.

Serafinavičius et al. [29] performed a four-point bending test on laminated glass specimens with three different interlayer materials: Trosifol (PVB), EVASAFE, and SentryGlas. They applied a sustained load at three different temperatures: 20 ºC, 30 ºC, and 40 ºC. The results from Figure 9 show that the midspan deflection was higher in specimens with PVB, which has up to 100 times lower stiffness properties than SentryGlas. Specimens with SentryGlas experienced the lowest deflection, closely followed by specimens with EVASAFE. In addition to the initial deflection after the application of the load, the deflection kept progressively increasing due to the creep of the interlayer. PVB experienced creep at all tested temperatures. SentryGlas and EVASAFE had better resistance to creep at low temperatures, but also experienced creep at higher temperatures, especially at 40 ºC. The results show how the viscoelastic behaviour of the interlayer material affects the cohesive behaviour of laminated glass.

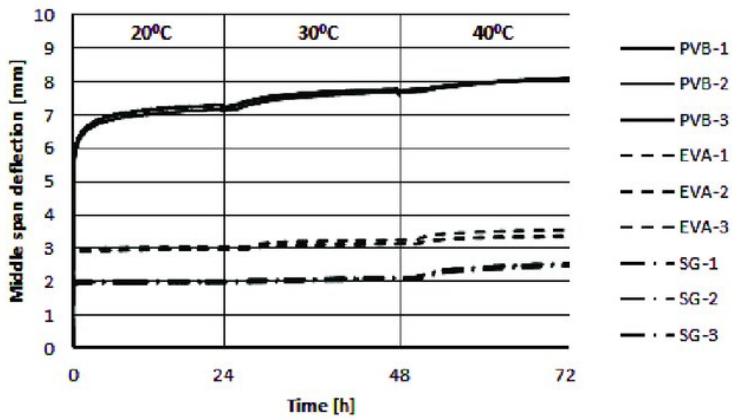

Figure 9. Midspan deflection of laminated glass panels, with three different interlayer materials, under long-term loading, and at three different temperatures [29].

4.1.2. Influence of load duration and working temperature

The behaviour of viscoelastic materials is a combination of elastic response, governed by Hooke's law (Equation 1), and viscous response, governed by Newton law (Equation 2). The more basic models to define the viscoelastic behaviour of a material are the Maxwell model, where an elastic element is connected in series with a viscous element (Equation 3), and the Kelvin-Voigt model, where an elastic element is connected in parallel with a viscous element (Equation 4). In the generalized Maxwell model (Figure 10), several Maxwell models are connected in parallel, allowing better adjustment of the model to the real viscoelastic behaviour.

$$\sigma_e = E \cdot \varepsilon_e \quad \text{(Equation 1)}$$

$$\sigma_v = \eta \cdot \frac{d\varepsilon_v}{dt} \quad \text{(Equation 2)}$$

$$\frac{d\varepsilon}{dt} = \frac{1}{E} \cdot \frac{d\sigma}{dt} + \frac{1}{\eta} \cdot \sigma \qquad \text{(Equation 3)}$$

$$\sigma = E \cdot \varepsilon + \eta \cdot \frac{d\varepsilon}{dt} \qquad \text{(Equation 4)}$$

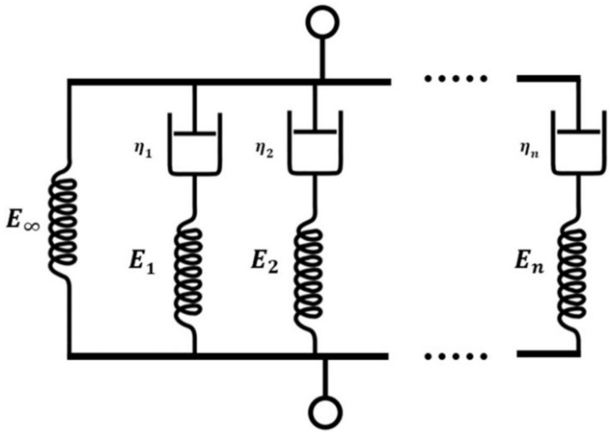

Figure 10. Representation of the generalized Maxwell model [108].

Instead of having a single, invariant modulus of elasticity, the mechanical behaviour of viscoelastic materials is defined by the complex modulus (E* or G*), which has two components: the storage modulus (E' or G'), associated to the elastic energy stored by the material, and the loss modulus, associated to the energy lost by the material, mainly in form of heat, due to its viscous part. At low temperatures and short-term loading, the elastic component is predominant, whereas at higher temperatures and long-term loading, the viscous component is predominant.

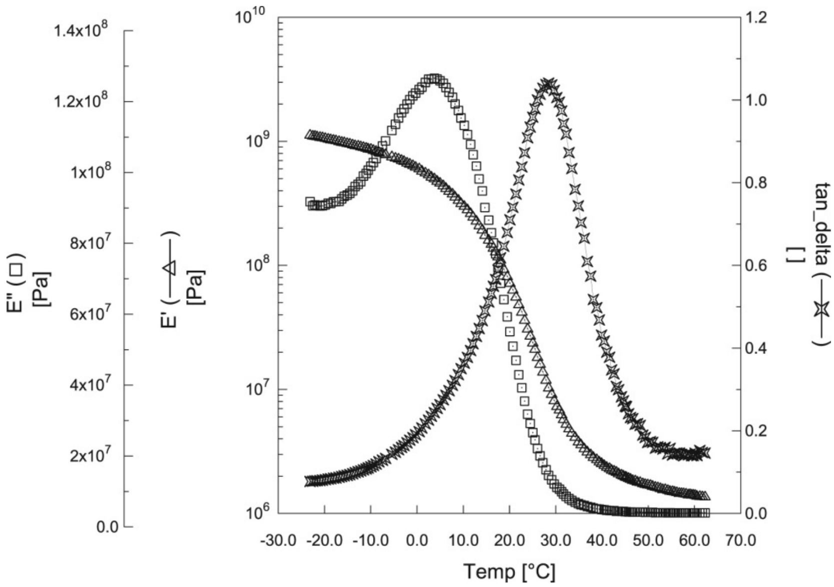

Figure 11. Storage modulus (E'), complex modulus (E''), and offset angle (tan(δ)=E''/E') of PVB obtained using DMA [108].

Increasing the working temperature and increasing the load duration have an equivalent effect on the mechanical response of viscoelastic materials: both lead to a reduction of the storage modulus and the complex modulus. This can be seen with the relaxation curves of the material at different temperatures. The master curve defines the mechanical behaviour of a material at a reference temperature and can be obtained by relating the relaxation curves at different temperatures using the time-temperature superposition.

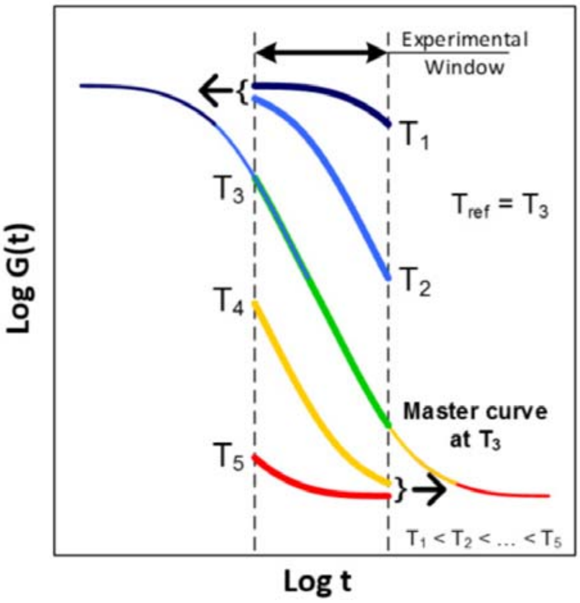

Figure 12. Schematic relaxation curves at different temperatures and master curve at the reference temperature T3 [114].

Different international standards describe the experimental procedures that can be followed to analyse the viscoelastic properties. For example, the EN ISO 6721-2011 [103] introduces dynamic methods for the experimental determination of polymer mechanical properties. The draft standard prEN16613:2013 [103] is related to the determination of interlayer mechanical properties and provides different methodologies to respond to specific problems of each interlayer.

In 2017, Giovanna et al. [105] reviewed the tests methods used in the literature for the determination of viscoelastic properties of interlayer materials. The study pointed out that, even though each method has its strengths and weaknesses, using a more reduced number of tests could help obtain a larger number of comparable experimental results. As the review mentions, the availability of different equipment in research laboratories probably determined the experimental campaigns. However, mechanical tests can be divided in two main groups: tests carried out imposing loads or displacements and dynamic transient tests. Tests carried out imposing loads or displacements at a given rate allow to quickly compare different materials or damaged specimens, whereas dynamic or transient tests are more adequate to characterize time dependent behaviour, specially creep and stress relaxation tests, which analyse long-term mechanical behaviour. Another important point that should be taken into account is the post-breakage behaviour of laminated glass and how the interlayer performs at this stage.

4.1.3. PVB

PVB is considered an isotropic, incompressible and linear elastic material [107]. For small deformations, linear viscoelasticity is a suitable model to describe its mechanic behaviour, where stress increases as function of strain in an exponential way. Liu et al. [58] demonstrated PVB strain rate-dependent behaviour in both tensile and compression tests. Under dynamic tensile loading, PVB behaves like an elasto-plastic material, while under tensile quasi-static loads its behaviour is viscoelastic. In the compression case, it presents viscoelastic behaviour in both dynamic and quasi-static loadings. Moreover, PVB constitutive model was defined and divided into three stages: linear-elastic stage, bi-exponent-like stage and failure stage.

Several dynamic experiments have been carried out to understand PVB mechanical response, such as the one carried out by Andreozzi et al. [42] with a rheometer. However, the widely accepted method to study polymer mechanical behaviour influenced by time and temperature is the DMA. This technique was used to find that between 0 ºC and 50 ºC PVB is in glass transition region. Therefore, its dynamic modulus presents remarkable variations with temperature and frequency. In contrast, in the glassy state, PVB presents brittleness and slight variations of the dynamic modulus as function of these parameters [59]. Following a similar procedure Pelayo et al. [108] found the beginning of the glass transition zone at 8-10 ºC. Additionally, frequency and time mastercurves were obtained throughout the William-Landel-Ferry (WLF) Time-Temperature Superposition (TTS) model.

The level of plasticiser on PVB affects its glass transition temperature and, therefore, its stiffness at a given temperature. The mobility between polymer chains is higher as temperature increases. This change from impaired mobility to free mobility of the polymer chains happens especially in the glass transition region. By increasing the concentration of plasticiser, the mobility between chains increases and starts at lower temperatures, meaning that the glass transition temperature decreases. Structural PVB, such as PVB ExtraStiff by Kuraray, has a lower amount of plasticiser compared to standard PVB. Figure 13 presents the relaxation curves of standard and structural PVB. These results show how, under a given load duration and working temperature, structural PVB has a higher stiffness than standard PVB. Figure 14 shows the master curves of both materials at a reference temperature of 10 ºC, obtained using the time-temperature shifting CFS algorithm [109]. The most significant decrease of stiffness corresponds to the transition from a glassy to a rubbery behaviour and such transition happens earlier for standard PVB than for structural PVB.

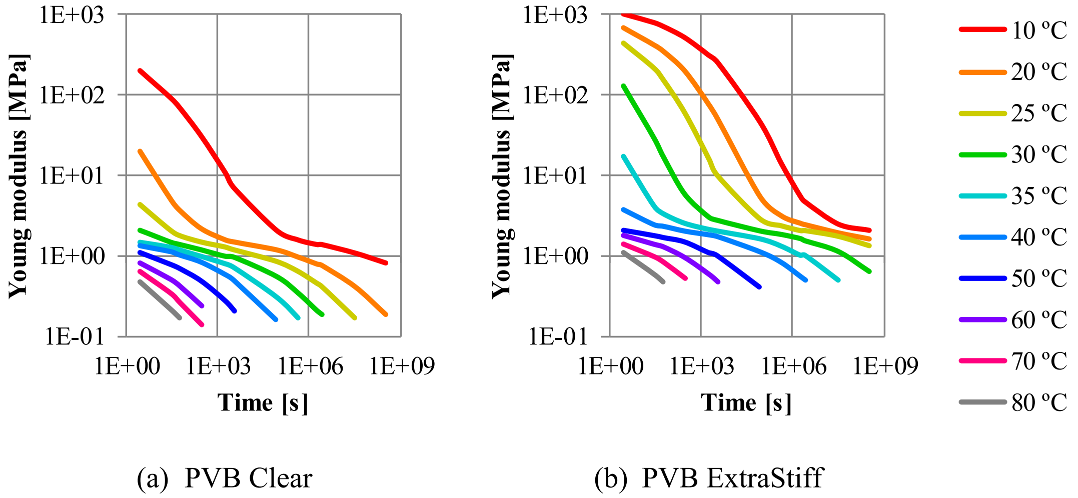

Figure 13. Relaxation curves of (a) PVB Clear and (b) PVB ExtraStiff at different temperatures. Data from the Kuraray data sheet (2018).

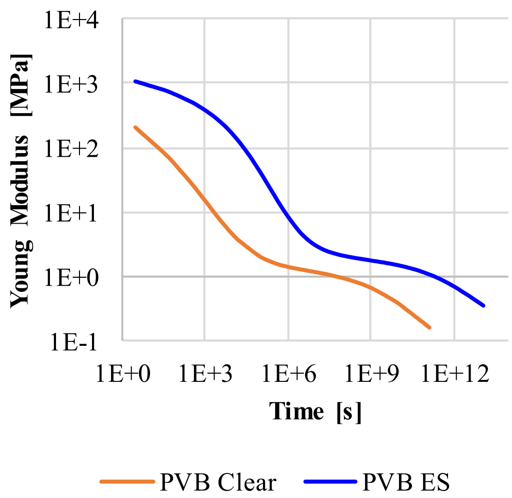

Figure 14. Relaxation master curve of PVB Clear and PVB ExtraStiff at a reference temperature of 10ºC, obtained using the time-temperature shifting CFS algorithm [109].

Another important mechanical aspect that has to be taken into account, according to prEN 13474-3 [110], is the shear transfer coefficient which quantifies the amount of horizontal shear force transfer by the interlayer to the glass plies. It is a coefficient with a value between 1 and 0, being 1 full shear transfer and 0 no shear transfer. Serafinavičius et al. [57] pointed out that shear transfer coefficient $\overline{\omega} = 0.5$ should be taken for PVB in short-term loadings instead of $\overline{\omega} = 0.25$, recommended by the standard prEN 13474-3 [110].

4.1.4.SentryGlas

The ionomer SentryGlas is a polymeric interlayer that was initially developed for high demanding applications, such as laminated glass exposed to bomb blast, burglary or hurricanes. This interlayer presents outstanding strength and stiffness compared to other interlayers, even at elevated temperatures. This makes it a widely used interlayer for laminated glass in structural applications. Figure 15 presents the relaxation master curve of SentryGlas compared to a structural PVB. Figure 16 presents the isochronal curves of SentryGlas and the same structural PVB. The results show how, at low temperatures and load durations, both materials present a similar mechanical response, but PVB is much more sensitive to load duration and temperature.

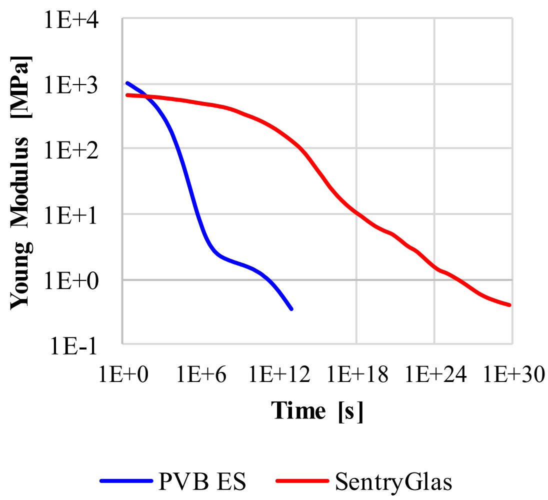

Figure 15. Relaxation master curve of PVB ExtraStiff and SentryGlas at a reference temperature of 20ºC, obtained using the time-temperature shifting CFS algorithm [109].

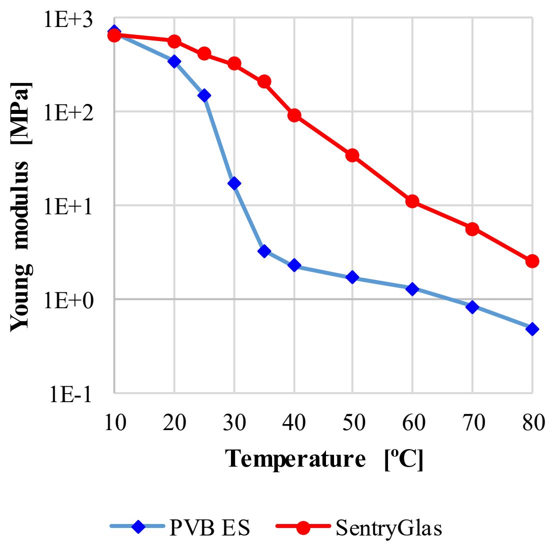

Figure 16. Isochronal curves of PVB ExtraStiff and SentryGlas for a load duration of 60 seconds.

An important advantage of SentryGlas is the structural coupling achieved between glass plies. Belis et al. [60] performed tensile tests with SentryGlas and demonstrated an elasto-plastic behaviour which is affected by strain rate. High strain rates provide higher yield stresses and more pronounced elongations. However, the strain rate did not have a noteworthy influence on the failure strength (above 32 MPa).

Zhang et al. [61] also performed tensile tests covering a wide strain rate range from quasi-static state (0.0056 s^{-1}) to high rate (up to 2000 s^{-1}). In this case, yield stress varied from 22 MPa at quasi-static strain rates to 47 MPa at high rates. The quasi-static tests showed a failure strain of about 400% while 2000 s^{-1} strain rate test presented lower failure strain (150%). This study derived the initial modulus of SentryGlas and found a value of 200-300 MPa at low strain rates and 150 MPa at high strain rates. Furthermore, the recovered deformation increases with strain rate.

Serafinavičius et al. [57] demonstrated negligible sliding displacement of SentryGlas laminates compared with other interlayers (PVB and EVA). Moreover, in the case of SentryGlas , the use of shear transfer coefficient $\omega = 1.0$ is recommended [57], being the interlayer with the highest value).

4.1.5. EVA

EVA mechanical behaviour presents an important dependence with VA content (4-40wt.%). Typically, a higher VA content leads to a more rubber-like behaviour. Therefore, low VA contents provide flexible and soft materials. Usually, EVA interlayers contain between 32wt.% and 34wt.% of VA, showing an intermediate performance between both described behaviours. However, EVA might change its mechanical properties significantly after the lamination process with glass. In order to study this phenomenon, Sable et al. [62] performed tensile tests on EVA specimens exposed to different lamination processes. Specimens heated for a three hours cycle at 120 ºC, following a similar procedure to one applied in industrial scale production, showed higher mechanical properties: 400% failure strain and failure strength of 12 MPa. It is also important to note that the linear part is similar for all considered processes. EVA presents better shear transmission in laminated glass components than PVB. Serafinavičius et al. [57] recommended the use of shear transfer coefficient ω=0.7 in short-term loadings. Moreover, this study showed that the ultimate loads of laminates with EVA and PVB interlayers were similar.

4.2. Ageing resistance

The term ageing refers to any irreversible physical and chemical process, which leads to a change in material properties and, thus, the applicability of the material is reduced over time. Degradation may affect the interlayer material transparency, mechanical properties, and adhesion with glass or other materials.

It is well-known that weathering conditions cause polymer premature degradation, affecting dramatically its main properties [95,96]. Therefore, the durability of laminated glass properties against weathering agents is a key factor to ensure suitability for safety design purposes. The agent of weathering of most concern to polymers is ultraviolet radiation (UV), although it is usually combined with the effect of other agents such as temperature, moisture, and oxidation. Accelerated tests can be carried out to study how each weathering agent affects polymers. Climatic tests combine weathering agents in a realistic accelerated ageing process. In current laminated glass design standards, factors such as glass surface quality, loading type and duration, and temperature effects are mentioned and evaluated deeply. Moreover, humidity, ultraviolet radiation, and temperature are also considered in international standards [97]. Nevertheless, it must be noted that this standard aims at determining the eventual appearance of faults (delamination, bubbles, etc.) that can be observed by visual inspection but do not aim at determining possible modifications in the interlayer material properties. For this reason, several authors such as Serafinavičius et al. [29,44,57] and Andreozzi et al. [42,43,51], undertake to study this weathering effect in the polymeric materials, basing its ageing tests in this standard.

Different ageing methods may lead to different changes in the material properties; that is why it is important to use standardized methods in order to be able to compare results. The different ageing methods found in the literature, standard and non-standard procedures, are listed, described and classified in the following sections.

4.2.1. Humidity tests

Depending on the chemical nature of the polymer, an interlayer can incorporate great quantities of moisture. PVB, for example, due to its significant proportion of polar alcohol groups is a hygroscopic material, which means it easily increases its water content when exposed to ambient humidity. Since water, which is a highly polar compound, holds bonding sites available on glass surface, a progressive reduction of adhesive bond-strength is observed with increasing moisture [18]. The reduced bonding properties due to the presence of moisture would have a negative effect on the post-fracture performance. For instance, the water content in PVB must be kept below 0.5% in order to maintain a suitable adhesion in the long term [46]. Optical properties may also be affected by ageing: a PVB sheet with 2-3% of water content decreases light transmission presenting serious white haze. This phenomenon increase with higher contents of free hydroxyl groups in the PVB chain [86]. Tupý et al. [86] also observed that the accurate critical value of water content is dependent on the type and content of alkali metal ions and alkaline-earth metals.

Table 6 summarizes interlayer materials studies regarding the effect of moisture; information about the humidity conditions, test duration and test performed to evaluate the effect of water is given. It is necessary to take into consideration that UNI EN ISO 12543-4 [97] establishes two test conditions for humidity tests. The first one with condensation; in order to ensure 100% RH, samples are kept vertically over water in a closed container. The second test, without condensation, utilizes a climate chamber at 80±5% RH. In both cases, humidity tests should last for at least two weeks. Taking into account this standard, several studies have been carried out in order to deeply characterize interlayer humidity resistance and improve it.

Delincé et al. [27] studied the effect of weathering on durability of laminated glass with PVB and SentryGlas from a mechanical point of view (shear and flexural tests). From the shear and flexural tests, adhesion and stiffness can be quantified respectively. The adhesion appears to be slightly reduced after exposure to weathering, while the stiffness appears to be slightly increased in both materials. In addition, it is noticed a qualitatively similar failure behaviour under static loads for PVB and SentryGlas in terms of adhesion of broken glass pieces to the interlayer.

In a 2013 study, Serafinavičius et al. [44] determined how glass laminated with different interlayer materials withstands the effect of humidity over 14 days. In this case, long-term bending tests at different temperatures, with loading perpendicular to the glass panel, showed that humidity has a minimum impact on the middle span deflection. Andreozzi et al. [51] tested the PVB humidity response setting samples over a thermostatic bath for extended periods of time (over 220 days). Delamination has been found only in samples exposed to humidity for extended periods of time. Changes in the bulk response of PVB were also found, concluding that further investigations are required to separately analyse these features. Prior to this, Louter et al. [28] performed studies concerning SentryGlas , confirming delamination phenomena and a significant reduction in bond-strength after moisture exposure; however, this was not reflected in the bending test. This may be due to the fact that in-plane loads were applied and the lateral displacement was prevented with lateral supports, which means that there was no relative displacement between adjoining surfaces, and therefore the interlayer material did not contribute to the structural performance of the composite sandwich material. Different moisture conditions have been applied in order to simulate glazing systems such as internal glazing, vertical and horizontal external glazing by Butchart et al. [52]. Results obtained showed that in presence of water the force required to peel PVB from the glass was less than half the force recorded under dry conditions. On this study the authors also highlight the importance of developing full-scale testing methods which distinguish between internal and external glazing. No studies were found regarding humidity resistance of the TPU interlayer materials.

Table 6. The effect of humidity on interlayer materials.

Reference	Materials	Humidity conditions	Test duration	Evaluation test	Year
Delincé et al. [27]	PVB	Based on UNI EN ISO 12543-4 [97] with condensation	360 hours (15 days)	Shear test (CST/TST) 4-point bending test	2007
	SentryGlas				
UNI EN ISO 12543-4 [97] (Humidity tests)	Laminated glass	100% RH: Samples vertically over water in a closed container (50^{+5}_{0} °C, with condensation)	336 hours (14 days)	Visual inspection (300-500 mm)	2012
		80±5% RH: Climate chamber (50^{+5}_{0} °C, without condensation)			
Louter et al. [28]	SentryGlas	Based on UNI EN ISO 12543-4 [97] with condensation	672 hours (28 days)	Pull-out test and bending test	2012
Butchart et al. [52]	PVB	3 different exposure levels: A. Sheltered, B. Exposed Drain C. Exposed subject to ponding	A and B not specified. C, 5 days.	Peel test (ISO 8510-1:1990)	2013
Serafinavičius et al. [44]	PVB/PVB plasticised	Based on UNI EN ISO 12543-4 [97] with condensation	336 hours (14 days)	Long-term bending test [111](EN 1288-3)*	2014
	SentryGlas				
	EVA				
Andreozzi et al. [51]	PVB	Based on UNI EN ISO 12543-4 [97] with condensation	456, 809, 5425 hours (19, 34, 226 days)	Visual inspection Thermo-viscoelastic properties	2015

*EN 1288-3 describes four-point bending setup. Serafinavičius et al. [44] conceive "Long-term bending test" (24h 20 ºC, 24h 30 ºC, 24h 40 ºC) at 50% RH (climatic chamber).

4.2.2.Solar radiation tests

Exposure to UV radiation (wavelength 10-400 nm) may cause photooxidative and photolytic reactions on most of organic-based polymers. Although the higher energetic part of UV radiation is filtered by the stratosphere, these reactions are able to break down the chemical bonds in a polymer, produce free radicals, reduce molecular weight and modify its structure, resulting in yellowing and mechanical property loss (cracking). Thus, exposure to UV radiation may modify the properties of laminated glass components, where polymeric interlayer materials are widely used. Nowadays a wide variety of stabilizers are available and used in commercial products: photostabilization of polymers might be achieved throughout many systems such as light screeners, UV absorbers, excited-state quenchers or peroxide decomposers [98].

Laminated glass durability normative, UNI EN ISO 12543-4 [97] considers simulated solar radiation tests and establishes possible radiation sources that provide a total irradiance level in the plane of the test of 900±100 W/m^2. From the literature review it was observed that the most common methodology used as reference is UNI EN ISO 12543-4 [97] with radiation spectrum similar to sun (method A). Table 7 shows solar radiation studies performed to the interlayer polymers indicating the radiation source, material, test duration, and how the effect of radiation is evaluated.

Table 7. Studies regarding solar radiation tests in interlayer materials.

Reference	Material	Radiation source	Test duration	Evaluation	Year
Delincé et al. [27]	PVB SentryGlas	Based on UNI EN ISO 12543-4 (A)	1000 hours <50 ºC	Shear test (CST and TST) and 4-point-bending tests	2007
UNI EN ISO 12543-4 (Radiation tests)	Laminated glass	A. Similar to solar radiation B. Wavelength of 300 to 450 nm	2000 hours (83 days) (45 ± 5) °C	Visual inspection (300 – 500 mm)	2012
Serafinavičius et al. [44]	PVB SentryGlas EVA	Based on UNI EN ISO 12543-4 (A)	2000 hours 45 ºC 50% RH	Long-term bending test (EN 1288-3) [111] (72 h)	2014
Andreozzi et al. [51]	PVB	Based on UNI EN ISO 12543-4 (A)	912, 7968 and 11209 hours	Visual inspection. Thermo-viscoelastic properties	2015

Delincé et al. [27], in 2007, investigated experimentally the effect of artificial weathering by mechanical tests (CST and TST) on PVB and SentryGlas laminated glass samples. Tests lasted for 1000 hours and a standardized UV radiation source was used. On the one hand, no defects according to the visual evaluation criteria of the standard were noticed for the tested samples. On the other hand, mechanical results showed a slight increase in the materials stiffness (TST) and a slight decrease in the materials adhesion (CST). Moreover, the failure behaviour of both interlayers under static loads seemed to be qualitatively similar.

UV radiation was also identified as a hardening agent in laminated glass with PVB, SentryGlas , and EVA by Serafinavičius et al. [44]. Long-term bending tests, with the loading perpendicular to the glass panel, were carried out to measure the effects of ageing on the interlayer material properties. After a loading time of 72 hours, the middle span deflection was practically the same for both aged and unaged samples; SentryGlas showed the lowest level of deflection during the whole experiment.

Lastly, UV radiation effect on PVB was studied by Andreozzi et al. [51] for longer periods of time. After visual inspection, rheological properties were measured. The study demonstrated that UV radiation is able to modify the structure of PVB, as it modifies the interlayer master curves shape (shear modulus). These changes have a direct effect in the long-term structural behaviour (creep and stress relaxation).

4.2.3. Temperature tests

The purpose of temperature tests is to determine if the interlayer materials are able to withstand exposure to high temperature over an extended period of time without altering their properties considerably.

Temperature tests are taken into account in UNI EN ISO 12543-4 [97], which consist of isothermal test at 100 ºC during either 2 or 16 hours in an oven or on boiling water. Temperature affects the viscoelastic response of the interlayer, but in order to simulate thermal ageing, most authors choose dynamic methods rather than isothermal tests. Dynamic methods, which include cycles between at least two temperatures, simulate better the ageing effects of temperature and are the most widespread methods in this field [28,51,53-55] and in other fields such as polymer matrix composites [99]. Table 8 shows temperature test studies, along with analysed materials, temperature program followed, test duration, evaluation method and year of publication.

Table 8. Temperature ageing tests for interlayer materials.

Reference	**Material**	**Temperature program**	**Test duration**	**Evaluation**	**Year**
Nabil et al. [53]	PVB	Test between 50-200 ºC	6 hours	FT-IR and viscosity measurements	1995
Weller et al. [54]	PVB SentryGlas	Isothermal: 120 ºC and 150 ºC TGA: 0 - 750 ºC	41 hours	TGA and FTIR	2010
Louter et al. [28]	SentryGlas	Cycles between -20 and +30 ºC Isothermal tests: 5 days at -20, +23, +60 and +80 ºC	150 cycles	Pull-out and bending tests.	2011
Kothe et al. [55]	PVB SentryGlas EVA TPU	Steps from 100 to 150 (based on EN ISO 12543-4)	Initially 16; all other 1 hours	Visual and luminous characteristic (light transmittance)	2011
UNI EN ISO 12543-4 (High-temperature tests)	Laminated glass	(100 ± 2) °C	A. 16 hours B. 2 hours	Visual inspection (300 – 500 mm)	2012
Serafinavičius et al. [46]	PVB SentryGlas EVA	20, 30 and 40 ºC (50% RH)	Testing time: 72 hours	Long-term four-point bending test following the scheme set by standard EN 1288-3 [111]	2013
Serafinavičius et al. [44]	PVB SentryGlas EVA	UNI EN ISO 12543-4 (B) (100 ºC)	Ageing: 72 hours Testing time: 72 hours	Long-term bending test (EN 1288-3) [111]	2014
Andreozzi et al. [51]	PVB	Cycles between 10 and 50 ºC	114, 202 and 568 cycles	Visual inspection. Thermo-viscoelastic properties	2015

Nabil et al. [53] studied throughout infra-red spectroscopy and viscometer how temperature progressively degrades PVB, modifying its chemical structure and affecting its physical properties. IR spectroscopy results showed that the C=O, -OH and C-H bands are broadened and its intensity reduced as a function of temperature. In addition, the band corresponding to the cyclic acetal disappears when temperature reaches 100 ºC. Intrinsic viscosity of PVB decreases constantly as function of temperature. This indicates that main chain scissions, instead of cross-linking, control the thermal degradation process. The authors also propose a possible degradation mechanism where degradation starts at the weakest points (acetate groups).

Different thermal stability tests were carried out by Weller et al. [54] to PVB and SentryGlas interlayers. On the one hand, isothermal experiments carried out at 120 ºC and 150 ºC during 2500 minutes showed that PVB lost 8% and 27% of mass, respectively. On the other hand, SentryGlas only lost 0.7-0.8%, respectively. TGA were also performed to both interlayers. PVB thermogram presented three different stages of decomposition (100 ºC, 150-330 ºC and 320-420 ºC). In contrast, SentryGlas showed a higher performance with only one stage that started at 330 ºC and ended at 600 ºC with a mass loss of 96%. It must be taken into account that the performance of the interlayer within laminated glass can be very different from the performances of the interlayer out of laminated glass.

Some authors studied the temperature effect on reinforced laminated glass, such as Louter et al. [28] who reinforced laminated glass beams with stainless steel sections. From their results both high and low temperatures (with respect to room temperature) affect negatively the laminated glass performance of these beams, especially in the post-breakage stage. The explanation for that is that the interlayer material, in the case of beams with in-plane loading and no lateral displacement, has a higher contribution to the structural performance after the breakage of the glass panels. At -20 ºC the interlayer could provide only a limited elongation at break, in contrast to +60ºC, when the deformation capacity is larger causing higher stresses in local points and debonding phenomenon. The study also pointed out that, for the geometry investigated in this study, thermal cycling had not noteworthy effects on the structural performance of the beams.

Kothe et al. [55] studied luminous characteristics (transmission values in visible and UV range) of thermally aged interlayers (PVB, SentryGlas, EVA and TPU), pointing out that no significant changes were observed in the visible range, transmission values vary from 85% to 95%.

Long-term four point bending tests were applied to glass beams laminated with PVB, SentryGlas and EVA by Serafinavičius et al. [29] where the length between the supporting rolls was 1000 mm. Middle span deflections, volatile displacements between the two glass sheets and longitudinal strains at different temperatures were measured. Deflection values increased with temperature, especially with PVB: from average 7 mm at 20 ºC up to 8 mm at 40 ºC. In contrast, SentryGlas showed the lowest deflection of all tested materials under different temperature conditions. The authors pointed out the relatively good results for EVA interlayer laminates, which presented a similar behaviour to SentryGlas. Slightly higher middle span deflections were obtained after thermal ageing, 2 hours at 100 ºC, for all interlayer materials [44].

Andreozzi et al. [51] found that the PVB rheological response is located in the rubbery dynamic region and thermal cycles performed under defined conditions (Table 9) do not affect this response significantly. From these studies, it was possible to identify a need to homogenize the testing methodology, given the lack of consensus over which testing methodology is the most adequate.

4.2.4. Simultaneous ageing tests

Although weather agents can be easily analysed separately, real conditions involve different weather agents acting simultaneously. Esslen [112] studied the effect of UV radiation, moisture, and air temperature on the shear strength, adhesion, and optical properties of PVB interlayer. In order to investigate the combination of these environmental conditions, several authors proposed alternative tests which combine different weather agents at the same time. Kothe et al. [55] performed climatic tests combining temperature and humidity, based on ISO 9142 [100] in three different climatic zones. This study includes four interlayer materials (PVB, SentryGlas, EVA and TPU) and evaluates degradation throughout IR spectroscopy, Dynamic mechanical analysis (DMA) and luminous characterization. Results showed no change in standard PVB properties below glass transition, nevertheless, the stiffness of the aged samples decreased significantly when temperature shifted above glass transition (>30 ºC). Miller et al. [56] exposed EVA laminates to UV radiation, relative humidity and temperature (Table 9) and evaluated systematically the combination of weather agents throughout CST, optical imaging and SEM. Results pointed out the condition-sensitive effect of simultaneous weather agents. For instance, at 80 ºC the loss of strength was much greater than at 60 ºC. In the case of humidity, 50% RH presented significantly different results compared to 30% RH. Therefore, the standards have to consider service temperature and relative humidity. Moreover, UV effects are at least comparable to the hydrothermal degradation produced by temperature and moisture.

Table 9. Test combining simultaneous ageing factors.

Reference	Test	Material	Tests conditions	Test duration	Evaluation	Year
Kothe et al. [55]	Climatic	PVB SentryGlas EVA TPU	3 climatic zones: a) 40 ºC at 95% RH b) -20 ºC at 20% RH c) 80 ºC at 50% RH (based on ISO 9142 [100])	15+2+4 hours	Visual and luminous characteristic (light transmittance), infrared spectroscopy, and thermo mechanical analysis.	2011
	Corrosion	PVB SentryGlas EVA TPU	ISO 9227 [101], saline atmosphere, 35 ºC	21 days		
Serafinavičius et al. [44]	Climatic	PVB SentryGlas EVA	UNI EN ISO 12543-4 [97]	2 (temperature), 336 (humidity), 2000 (UV) hours	Long-term bending test (EN 1288-3 [111])	2013
Miller et al. [56]	Climatic	EVA	1.0 $W \cdot m^{-2} \cdot nm^{-1}$ at 340 nm Xe and UVA-340 sources. 60 ºC, 30 and 60% RH.	15, 30, 45, 90, 135 and 180 days	Compressive shear test (CST) constant strain rate of 0.05 s^{-1}	2016

4.3. Discussion

The mechanical behaviour of each interlayer material depends on its composition. For instance, EVA with a lower content of VA is more flexible and softer, and the amount of plasticiser in PVB affects its glass transition temperature, which has a direct impact on the strength, stiffness, and viscosity of the material.

Several tests are carried out to determine the mechanical properties of interlayer materials and laminated glass (Table 10). In these tests, it is essential to specify the strain rate, load duration and working temperature, since these parameters may affect the results, given the viscoelastic behaviour of the interlayer materials. Out of all the tests evaluated, DMA tests were the more adequate to characterize the time- and temperature-dependent behaviour of the interlayer material, both within and outside laminated glass.

Table 10. Mechanical tests for interlayer materials.

Material	Reference	Measured parameter	Test	Test conditions	Year
PVB	Liu [58]	Stress – strain curve	Tensile strength test	4 quasi-static loading: $4\cdot10^{-3}$, $2\cdot10^{-2}$, $4\cdot10^{-2}$ and $8\cdot10^{-2}$ s^{-1}	2012
			Compression test	$4\cdot10^{-4}$, $4\cdot10^{-3}$, $4\cdot10^{-2}$ s^{-1}	
	Serafinavičius et al. [57]	Failure load, middle span deflection and sliding displacements	Four-point bending tests (EN 1288-3) [111]	22 ºC	2013
	Andreozzi et al. [42,43] Liu et al. [59] Pelayo et al. [108]	Storage modulus (E'), loss modulus (E''), Phase angle δ, tan δ=E''/E'	DMA	There are 21 groups of experiments covering temperature (223 – 323 K) and frequency (0.01 – 80 Hz).	2014
SentryGlas	Belis et al. [60]	Stress – strain curve	Tensile test	5 different loading speeds (5, 10, 20, 50, 100 mm/min)	2009
	Serafinavičius et al. [57]	Failure load, midspan deflection and sliding displacements	Four-point bending tests (EN 1288-3) [111]	22 ºC	2013
	Zhang et al. [61]	Initial modulus, yield stress and strain, failure stress and strain	Tensile test	Strain rate: 1. Low speed tests 0.0056 s^{-1} to 0.556 s^{-1} 2. High speed tests 10 s^{-1} to 2000 s^{-1}	2015
EVA	Serafinavičius et al. [57]	Failure load, mid-span deflection and sliding displacements	Four-point bending tests (EN 1288-3) [111]	22 ºC	2013
	Sable et al. [62]	Stress – strain curves	Tensile test	ASTM D638 applied to different level of heat treating, up to 3 h/120 ºC	2017

There are many parameters that must be taken into consideration when choosing the most adequate test for each application: first, one must know what information can be extracted from each test. Tensile and compressive tests, as well as viscosity measurements, provide information about the interlayer out of laminated glass. However, the properties of the interlayer may change during the lamination process; therefore, these tests may provide useful but incomplete information. Bending, shear or peel tests on laminated glass specimens are better to evaluate the global behaviour of laminated glass as a composite laminate. However, these tests do not consider the time- and temperature-dependant behaviour of the interlayer, while dynamic tests (DMA) does. The cost of the specimens for each test may depend mainly on its size and the manufacturing process. Specimens that can be fabricated using the same method as final parts are preferable in order to better extrapolate the results. In addition to the cost of the specimens, there is the cost of the equipment. The price may vary depending on the size, accuracy, and working range. For small specimens, the universal machine can do tensile and compressive tests. With special clamps it may also perform bending or shear tests. This test equipment is generally cheaper than DMA systems, which is very accurate and contains a climate chamber, and bending test benches, which are generally bigger.

Interlayer materials for laminated glass must be transparent and have a good level of adhesion with glass. The importance of some other requirements may depend on its final application, such as the capacity to absorb impacts, act as a thermal or acoustic insulator, resist weathering factors, or transfer shear loads between glass layers.

The most important parameters of the interlayer material regarding post-breakage performance, according to Delincé et al. [106], are stiffness under static conditions and toughness under dynamic conditions. Another important factor for the post-breakage safety of laminated glass is the level of adhesion at the interface. The interlayer may contribute to bridge the cracks, prevent them from propagating, and avoid the projection of glass shards. However, that can only happen if there is adhesion between glass and interlayer at the cracked region.

The exposure to ageing factors may affect the transparency, strength, and stiffness of interlayer material, as well as its adhesion with glass. In order to simulate the exposure to weathering factors, some tests combine different ageing factors (humidity, UV radiation, thermal cycles, high temperature), whereas some others simulate each factor separately. The simultaneous exposure to several factors describes more accurately real life conditions but studying them isolated allows to identify the effect of each of them separately.

5. Recyclability

The Roadmap to a Resource Efficient Europe (RERM) [115] highlighted construction as one of the three key sectors to be addressed. The study pointed out that better construction and use of buildings in the EU would reduce 42% of the final energy consumption, about 35% of the greenhouse gas emissions, and more than 50% of all extracted materials. It could also help to save up to 30% of water. The improvement in the efficiency of building materials life cycle will make the construction sector more competitive and reduce its environmental impact. This can also be extended beyond building materials, such as the automotive industry and solar energy sector. The environmental impact during the manufacturing process and the rest of the life cycle is higher for laminated glass than for toughened glass (thermally treated), and even higher compared to flat glass [116]. For that reason, there is a need to improve such processes and find new ways to revalorize the waste. Due to the clearly different nature of the two materials which constitute laminated glass, both have to be recycled separately. One the one hand, glass is separated from polymeric interlayers quite easily, and in terms of transparency it can be fully recycled unlimited times without any loss in purity or quality. On the other hand, polymeric interlayers present several difficulties, since they contain small contents of glass and water that impede the interlayer recycling [63,64]. The process of separating glass from interlayer in order to recycle them separately may have a significant impact on the recyclability of laminated glass.

Several studies focus on the design, development and optimization of a process for recycling interlayers from laminated glass from the main sectors (i.e. construction and automotive) [117]. Nevertheless, the literature investigation suggests that studies on recycling of interlayer materials are mainly focused in PVB, especially in automotive field (primarily windshields). This can be explained because PVB is the most used interlayer and laminated glass constitutes up to 3% of the total material in vehicles at the end of its useful life. As a result, every year in Europe more than 480,000 tonnes of laminated glass are arising from End-of-life vehicles (ELV) [117]. To the best knowledge of the authors, until now only one manufacturer offers interlayer sheets with a 100% recycled PVB (Butacite G from Trosifol). This material is manufactured from collected post-industrial PVB trimmings. After reprocessing the PVB, the obtained interlayer showed a decrease in its light transmission value: the light transmission drops about 0.2% after every reprocess cycle [86]. Considering that minimal commercial value is 89.5%, this degradation phenomenon might limit the number of times that PVB could be reprocessed. Even though European Union funded several projects [118,119] in order to fix this issue, most of this material is incinerated or buried and only a fraction is recycled.

Usually, recycling studies consider three main aspects: raw material, valorisation process and processed material. However, each published study focuses, to a greater or lesser degree, in one aspect, and this is qualitatively assessed in Table 11. In Table 11, available information in the literature is summarized and classified considering these three aspects. Recycling processes for the other interlayers were not found in the literature. For the sections that follow, special attention will be given to the recycling processes for PVB, since it is by far the most used and recycled interlayer.

Table 11. PVB recycling studies classified considering three main aspects: raw material, valorisation process and processed material.

Reference	Year	Raw material		Valorisation process		Processed material	
		Application	Characte-rization	Separation	Reprocessing conditions	Valorisation	Characte-rization
Dhaliwal [63]	2002	Automotive windshield	✓✓	×	✓	✓✓	✓✓
Tupý et al. [64]	2012		✓✓	×	✓✓✓	×	✓✓
Swain et al. [65]	2015		✓	✓✓✓	×	✓✓	✓
Burmistrov et al. [66]	2016		✓	✓	✓✓✓	✓✓	✓✓✓

Apparently, different commercial and recycled grades of PVB can be blended without incompatibilities and can be used as substitute material in glass lamination. Dhaliwal et al. [63] characterized PVB from a wide range of sources and companies (including recycled PVB), throughout NMR, GC-MS, DSC (T_g), TGA, and IR (ATR). Results showed that the blends and recycled polymer could be reused taking into account the similarity in chemical composition, mechanical response and plasticizer content compared to virgin PVB. Tupý et al. [64] studied re-processing conditions such as temperature, oxygen content, mechanical stress and PVB moisture content. Taking into account mechanical properties and MFI results, the optimal conditions for re-processing by kneading were 150 ºC and a rotation speed lower than 60 rpm (higher temperatures produced the yellowing of the material). The amount of water in the PVB sheet was pointed out as a critical parameter: water can act as an additional plasticizer improving workability; however, wet material was more prone to hydrolytic degradation. In 2015, Swain et al. [65] proposed a sustainable mechanical-chemical process to separate PVB from glass using non-ionic surfactants (D201). After parameter optimization, separation conditions considered optimum were 30 vol.% D201, stirring speed of 400 rpm, 35 °C and an operation time of 1 hour. Afterwards, processed PVB was deeply characterized by means of TGA, SEM with EDS, IR and NMR. However, it is also important to study the possibility of secondary PVB recycling. For instance, Burmistrov et al. [66] in 2016 investigated PVB material valorisation as composite coating. PVB wastes, offcuts of the windshield production, were modified with potassium polytitanate (PPT), obtaining films with high mechanical properties which can be used as wear resistance coatings. The characterization process gathered the viscosity of the PVB by means of glass capillary viscometer, the application of TEM, SEM with EDS, PSD techniques to PPT particles and the pull-off test (ISO4624:2002) for the new developed coating.

6. Conclusions

Nowadays most of laminated glasses are being made of PVB and, in a smaller proportion, SentryGlas and EVA. Several researchers have made efforts into developing alternative materials, mainly based on TPU, PMMA, PET, PC, and others. Now it would be necessary to However, further research on these alternative interlayer materials is needed in order have more understanding of how they behave in laminated glass, and how they respond when subjected to different loading scenarios, working temperatures and ageing factors. The fact that such information already exists for PVB, which has been a consolidated interlayer for many years, proves that the same research for other interlayer materials may be of interest for the laminated glass market.

Interlayer characterization techniques reported in the literature were diverse and were not properly standardized. One of the main issues to be solved regarding polymeric interlayer materials for laminated glass is its resistance to weathering conditions (i.e. ageing). The standard ISO 12543-4 [97] addresses laminated glass durability, but does not provide enough evaluation methods to study the effects of the ageing factors on the mechanical, optical and adhesive properties of the interlayer materials. It can be concluded that unanimous methodology has to be established in order to compare ageing studies with different materials. However, each weathering agent presents its own specific difficulties:

- Humidity: Interlayer water content, especially for PVB, might affect significantly its adhesion to glass. Experimental conditions should distinguish between internal and external glazing and consider polymer chemistry consideration. Based on the above, a well-defined methodology is needed, and long-term tests are required to show representative results. Authors provided studies which ranged from 5 to >220 days of exposure.
- Solar radiation: A more specific investigation on the damages produced by UV radiation in the polymeric materials has to be carried out in order to enlighten probable different degradation mechanisms, which alter the plasticizer and polymer matrix properties.

- Temperature: Dynamic and isothermal temperature tests are proven valid experimental methods to study PVB thermal ageing. However, there is a need of standardization in the procedures. Further research regarding other interlayer materials is also needed.

The mechanical performance of laminated glass has been largely studied, and viscoelastic models seem to be the best approach to characterize PVB mechanical response. DMA provides all the information necessary for a time- and temperature-dependent study. Nevertheless, only PVB and SentryGlas were fully characterized by the mechanical point of view, and therefore more studies regarding alternative interlayers (e.g. EVA and TPU) are required in order to use these materials in structural demanding applications. Interlayer material mechanical characterization techniques have to be limited to a reduced number of simple tests so that they can be done in more laboratories and different laboratories provide comparable results. Moreover, interlayer material studies taking into account temperature and time parameters should be made in order to gain valid data, which is crucial for component design and modelling.

From the gathered information, the authors conclude that PVB is the most commonly used interlayer material, but not necessarily the best for all applications. PVB presents a good level of adhesion with glass, as well as transparency after the lamination process. However, SentryGlas is stronger and stiffer than conventional PVB, and presents a good level of adhesion to both glass and metals, which makes it adequate for glass-to-steel connections in embedded joints, point-fixings, or laminated glass beams with steel reinforcements. The glass transition temperature of SentryGlas is also higher, and therefore it has better mechanical properties at higher temperatures as well. However, up until now, SentryGlas is still more expensive than conventional PVB. Laminated glass with EVA presented similar stiffness to SentryGlas, but more experimental results are needed to evaluate its performance under several working conditions. New versions of PVB are being developed with improved performance for certain applications. For example, compared to conventional PVB, Trosifol UltraClear presents higher level of transparency, Trosifol Acoustic has higher acoustic insulation, and Trosifol ExtraStrong is stronger and stiffer.

The authors identified that further research should be carried out on TPU, but its good mechanical properties, as well as its good level of adhesion to glass and polymers such as PMMA or PC, would make it a good candidate for composite laminates that combine glass layers with PMMA or PC layers. That combination allows obtaining bulletproof glass or safer transparent beams than the ones made with laminated glass.

Glass represents a large component of household and industrial waste due to its high weight and density. However, glass can be recycled as many times as necessary, without optical or mechanical degradation, and usable glass products could be made with over 90% recycled glass. On the other hand, from the interlayer materials recyclability point of view, lots of efforts are required find out better end-of-life practices and processes. The end-of-life behaviour of PVB interlayers should be also addressed for the specific case of the building sector in particular, since the use of laminated glass in construction components is experiencing a steady growth.

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