Polymers give added functions to toughened glass

This article summarises developments in liquid polymer laminating and coating applications for toughened glass production. Materials and processes for the manufacture of glass laminates with safety, security or sound reducing properties are reviewed and new developments in thin-film polymer-coating technology for the production of hydrophobic coated glasses are described. Moreover, application technologies are explained in as far as they are in the public domain, and principles of product assessment are also summarised.

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Laminating glass with resins

The concept of improving the performance of a material by combining two or more layers of either similar or dissimilar properties is a concept well proven in all industries; e.g., combining the properties of waxed carton with thin films of aluminium creates a packaging material so successful that its sheer universality and unit numbers are in fact causing an environmental problem. The most obvious benefit to be obtained from laminating glass is the containment of fractured pieces of glass, which implies a safety feature to those laminates whilst offering some structural integrity which could be important in preventing damage to a building by still providing an effective sealing function. The nature of the interlayer can influence the pattern
of fracture of (annealed) glass. Laminating multiple layers provides security, as well as bullet and blast resistant products. A relatively recent development was the creation of laminates with interlayers which modified the sound transmitting properties of glass in such a way as to significantly reduce sound levels whilst maintaining glass’s outstanding features, namely its clarity and visual properties. 

Lamination processes can be divided into two categories:
1. The interlayer is applied as a pre-formed, solid film (usually PVB, polyvinyl butyral, or polyurethane for specialist applications) and is adhered to the glass by heat and pressure in an autoclave which, by its sheer nature, involves a considerable investment in plant and equipment.
2. A liquid resin is introduced between two sheets of glass and is then caused to cure chemically, (either by the action of a catalyst or by the exposure to UV radiation) into a solid film, which may even exhibit chemical adhesion of the interlayer to the glass, forming a truly bonded composite. Again by this description it is suggested that the required investment will be smaller than with previously described processes. Often these processes are either used for very specialised applications or simply as a means to an end rather than as a fully streamlined process.

In both instances, however, exceptions are to be found which tend to confirm the rules.

A more useful differentiation between these processes is the analysis of the type of market segment into which the products of these processes are supplied. A simple standard safety laminate can be produced more cheaply using the autoclave process than a resin laminating process. Trying to laminate deeply patterned glasses or indeed toughened glasses using a solid pre-formed film can be a costly hit and miss exercise. A resin system is clearly more suited.

Resin systems are sometimes also seen as being a simpler, cheaper way of producing laminates which can actually reduce the entry level into laminating. This is probably one of the biggest fallacies prevailing. Successful industrial resin laminating requires a similar level of preparation, control and expertise as is required for PVB laminating. So if the process is not as simple as is often suggested, why bother? The answer lies in the diversity of applications for glass itself. By operating a resin laminating facility, the producer has instant access to any number of products which can be created from limited stock materials at short notice to satisfy customer needs. In some cases this is the only way a particular product solution can be achieved. Particular reference is made here to sound reduction laminates and the combination of patterned or otherwise uneven glass sheets.

**Chemical principles**

For a material to be suitable for laminating it must be clear (so as not to impair the main reason for using glass in the first place), has to cure to form an interlayer in situ which provides the required mechanical and physical properties and, lastly, has to maintain those beneficial properties over the lifetime of the product at reasonable cost.

From the large number of organic materials available only a small number are suitable. In the main, polyesters and acrylates and their derivatives dominate the market. These have in common that they all cure by similar radical induced mechanisms. The initial radical can be provided by some sort of peroxide (multi-component systems) which has to be mixed with a base resin at the correct ratio and which usually requires at least one other component which provides chemical adhesion via a silane based adhesion promoter. In some cases, additional components can be used to control the pot life of the mixed resin.

Single component systems carry all these functions within one package. The radical reaction is started by a compound called a photo-initiator which, when exposed to UV light, will form radical molecules which start the polymerisation process. The advantages are clear, no more dosing and mixing with the
resultant waste, simpler stock control and simpler machinery. These systems have to be designed really well; as by combining all the reactive components into one package, there is the potential for unwanted reactions between the constituents, rendering them individually ineffective and thereby impairing the whole function of the resin.

A typical laminating line will consist of a glass washing facility, an assembly area where the glass sandwich is made up (using double sided tapes which are compatible with resin to be used), a filling table which can be manipulated in two axes to allow the filled laminate to be de-aerated and then sealed. For the filling process, accurate dispensing equipment is strongly recommended. Manual dispensing and mixing is feasible only in the most controlled conditions. A curing area that needs to be flat yet allows laminates to be moved without disturbing the interlayer prior to curing rounds off the production line. In the case of single part UV curing systems, this curing area is supplemented by uniform sources of UV radiation (usually UV tubes).

The critical issues here include the flatness of the filling and curing facility, the accuracy of the metering pump, the uniformity and correct radiation level. Equally environmental conditions must be kept within reasonable bands to avoid a host of potential problems. After all, it is sensitive 'real' chemistry which is placed in what is usually an industrial environment not attuned to the requirements of complex chemical processes.

Well-trained personnel are critical to the success of an industrial laminating facility that is expected to produce high value, bespoke product at minimal risk. Above all, the advice of the material and equipment suppliers should be followed, where this is conflicting or simply unclear, clarification must be sought.

Typical performance levels of resin laminates

Depending on what level of safety performance is required, resin laminates are usually produced with thicker interlayers than PVB. This stems partly from the fact that it is difficult to produce uniform resin interlayers of less than 0.75 mm. Common interlayers range from one to two millimetres in thickness. Resin laminates generally will fulfil all the safety and impact testing requirements which are achieved by laminates made with PVB. The design will differ in most cases.

Of particular interest is the ability to laminate toughened glasses, which by the nature of the process, are distorted and therefore would be costly to laminate by other means. For example, applications could include overhead glazing where the interlayer is effective in containing the glass particles while still sealing the building. Potential exists for combining toughened solar control glass with a sound reduction function to provide a highly functional curtain walling element.

The effectiveness of an interlayer in reducing sound can be assessed very easily by viewing a sound level reduction versus frequency chart. By observing to what extent the coincidence frequency drop is shifted away from the theoretical frequency value (which is in the main a function
of the glass mass) the interlayers’ role (decoupling effect) in reducing the sound levels can be confirmed.

**Environmental stability**

As with all products intended for exposure to environmental influences, accelerated weathering testing in the laboratory is a mainstay of product development and subsequent assessment of products. Generally resin laminates perform well in terms of UV stability and resistance to colour change under heat ageing conditions. It must be appreciated however that all organic materials (including PVB) will at some point discolour provided the conditions are harsh enough. Acceptance levels must be defined, usually between customer and supplier as there are very few recognised standards that are meaningful in this context. One must be aware of the test conditions when comparing one set of test results with another. Correlation of accelerated weathering data with natural weathering data can obviously only be available if the tests have come to completion (25 year test data needs about 25 years to be gathered!)

One benefit of chemically bonded resin interlayers versus the physical adhesion of PVB is the increased resistance to delamination caused by moisture. Resin interlayers tend to go cloudy but will recover once the source of moisture is no longer present. PVB will usually delaminate in moist conditions.

**Thin film polymer coatings**

Glass is an inorganic material with unusual properties. As a solidified melt of mainly silica and various metals and metal oxides, glass exhibits high transparency and clarity as well as resistance to a wide range of aggressive media. Protect Glass? Why?

**Chemical principles**

Based on its chemical composition, the glass surface provides a polar substrate which is attractive for all water-loving (hydrophilic) substances. Due to the higher levels of glass processing and increased pollution levels, the glass surface finds itself exposed to increasingly aggressive external influences. It can therefore be assumed that glass surfaces will not only be contaminated to a higher degree but also result in a reduced lifespan of the surface.

‘Glass’ is generally associated with ‘smooth’. Taking a microscopic view, however, reveals...
a ‘rugged mountain landscape’. It is this topography which further encourages the depositing of water and dirt.

Yet, a glass surface is expected to cope with a lot: chemical attack by climatic and environmental agents such as moisture, acid rain, salt and fumes.

What is commonly classed as glass corrosion or leaching can be easily explained in principle. In this model, glass is viewed as a three-dimensional structure. At the surface such a structure cannot be formed, which is why reactive components of the silica oxide (Si-OH groups) make up the hydrophilic character of the glass surface.

Defined in chemical terms, glass corrosion implies that metal ions are removed from the structure and transported to the surface. At this point alkaline solutions are formed with residual humidity (e.g. caustic soda). Through this a further disassembly takes place which starts to affect the structure of the glass. The structure-forming silicoxide bridges are destroyed, the porosity of the surface increases and the corrosion develops further. A similar process may be initiated by acid rain (2, 3).

To clean such surfaces requires a much greater effort. Once the corrosion is visible then the surface has already been destroyed irreversibly.

To improve the glass surface in this respect, a chemical change in the surface is one possibility.

Such a modification is aimed at a reduction in the hydrophilic character of the surface or even a reversal to a hydrophobic behaviour on the one hand and a ‘smoothing’ of the surface on the other.

To this end two options are available:
1. Change of the surface chemistry and topography by coating with glasslike substances which are thermally fixed at high temperatures on the surface (Sol-Gel Process).
2. Modification of the surface roughness and/or the surface chemistry with a low-viscosity coating which is able to follow the topography; i.e. is able to attach active substances to the structure.

Option 1 will not be discussed here because of the high application effort and the resulting high costs.

With regard to option 2, further options can be identified:
a) coating the surface with non reactive ‘oily’ substances;
b) coating the surface with reactive monomers and/or oligomers.

The hydrophobic characteristics of the coated surface can be equally good or bad with either approach. The difference can be found in the durability of the coating.

Durability is linked here to the capability of the coating to form chemical bonds with the glass surface, i.e. bonding to the Si-OH groups.

Non-reactive coatings rely on utilising the topography i.e. the ‘hills’ and the ‘troughs’ in the surface are filled with requisite molecular structures. These molecules are able to form electrostatic interactions with the glass surface (physical adhesion). However, the effectiveness of these interactions is compromised by the presence of water.

In contrast to this, reactive systems are able to bond with the Si-OH groups chemically, which results in a strong and durable composite between glass and protective layer. If such a system is then able to form a network within itself, a closed, smooth and very thin protective coating is achieved.

**Evaluation methods**

Due to the minuscule thickness of such a layer, only a few millionths of a millimetre, the characterisation is difficult.

One has to rely in the main on phenomena, i.e. tests which indicate a change in the...
behaviour of the surface towards water for example. Such behaviour could be the geometrical shape of a water droplet on a surface.

The angle of contact represents such a measurable entity (Fig. 7) which can describe the hydrophobic character of a glass surface.

This method is an established tool used in surface analysis and is utilised mainly to describe surfaces after artificial ageing processes.

In practice, however this quantity only represents part of the picture. To achieve a reduction in soiling, a water droplet should not only wet the surface minimally but in addition it should run off easily.

To define this behaviour a suitable droplet run off apparatus was developed.

In evaluating Crystal Guard - a Chemetall GmbH product - comparative testing has revealed no significant differences in the angle of contact between Product ‘1’ and Crystal Guard. (Fig. 6)

The droplet run off test however reveals Crystal Guards advantages. The angle at which the droplet starts moving is clearly lower than coating ‘1’.

This measurement set-up also evaluates the surface topography. Generally it is advisable to consider the practical situation and choose the characterisation accordingly.

Based on this method wash cycle testing and accelerated weathering testing were commissioned with the TPD/TNO, Eindhoven, Netherlands to establish the durability of the coating. From experience with testing insulating glass units, a weathering test series was designed. Weather-O-meter (5), Saltspray (6), Acid气候 (7), Climate change(8) testing as well as cleaning tests with a standard glass cleaner and an abrasive cleaner was performed. The results were evaluated against defined, untreated sides of the samples.

The TNO (4) results are quoted as follows: “The following conclusions can be drawn from the research:

- The water repellent property of glass treated with Crystal Guard is greater than the same property of untreated glass;
- Following ageing, Crystal Guard retains this
property to a greater degree than that of untreated glass;
• Crystal Guard provides effective protection against the leaching that may occur during a climate change test;
• If the angle of the installed window is too low, the diffuse reflection due to the ring-shaped deposits left behind after drying may on average be greater;
• Where window installation is at an angle, new and untreated glass has a critical angle of >30 degrees relative to the horizontal. Where the glass surface is treated with Crystal Guard this angle is on average 5 degrees lower;
• Crystal Guard treatment generally results in less fouling of the glass surface. In practical situations this may mean longer intervals between successive washes;
• Subsequent to spraying with standard fouling, all samples, except for the salt spray test and the abrasion test show lower accumulation of fouling to glass surfaces treated with Crystal Guard relative to untreated glass;
• Washing a glass surface treated with Crystal Guard does not reduce the performance of the coating;
• Mechanical stress created by an abrasive cleansing agent on glass surfaces treated with Crystal Guard does not cause the water-repellent properties to deteriorate.”

Practical application

An impressive demonstration of the advantages of this technology is the case of the Estrelle Hotel in Berlin, Germany. An integral part of one of the largest hotels in Germany is an inclined roofing curtain-wall section which is in the immediate vicinity of a chocolate factory, a scrap yard, two airports and the city freeway system. The potential for soiling is very great at this location. The curtain-wall section can be cleaned with great difficulty as it is accessible only by rope.

In an attempt to resolve the situation, two rows of windows were cleaned in November 1996. Four panes of glass were treated with Crystal Guard. In March 1997, a clear visual difference was apparent. The treated panes were much cleaner and were found to be easier to clean. This demonstration was a success, so the whole curtain walling system has now been treated with Crystal Guard.

Similar results are reported from applications in the Netherlands. This leads us to believe that the chances for these specialised thin-film polymer coatings are significant and can offer an additional value-adding stage to glass processors, not only as a product for application in the factory but also as a retrofitting asset.

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