HARD-SOFT COMBINATIONS WITH SILICONE RUBBER-INNOVATIVE TECHNICAL SOLUTIONS

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Silicone Rubbers

The first silicone rubber products have been introduced into the market more than 50 years ago [1]. This was possible due to the unique properties of silicones (also known as polysiloxanes) based on their molecular structure with a silicon/oxygen backbone, where the remaining valences of the silicon atom are saturated by hydrocarbon radicals (mainly methyl groups). Silicones and silicone rubbers exhibit outstanding properties such as:

- high temperature resistance (up to 300 °C),
- maintenance of resilience even at low temperatures (down to –50 °C),
- temperature independence of physical properties in general,
- good aging stability and weather resistance,
- biological compatibility.

If necessary, these properties can be further improved by modifying the silicone polymers or by using special additives during compounding [2].
Silicone rubbers usually are classified either as Room Temperature Vulcanizing one and two component systems (RTV1 and RTV2) or High Temperature Curing rubbers (HV, HCR, HTV). The latter can be divided into High Consistency Rubber (HCR) which are normally processed in similar equipment to organic rubbers and the Liquid Silicone Rubbers (LSR). **(Fig.1)**

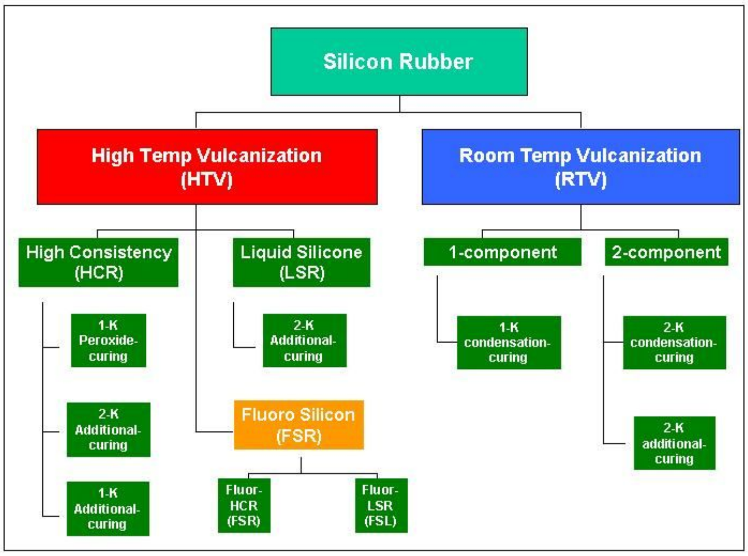

Figure 1: Classification of Silicone Rubbers

The LSR silicone polymers have a lower viscosity compared to the raw material of the high consistency rubbers. In contrast to HCRs, a modified injection molding process is used for LSRs, enabled by their lower viscosity as well as by their high reactivity based on a platinum-catalyzed hydrosilylation reaction [1].

Bonding Theory

Bonding can be either cohesive or adhesive. We understand cohesion as the sum of all interactions being responsible for the bonding of atoms and molecules within a solid or liquid. Adhesion covers all interaction in the interface of two phases sticking together. As a matter of fact in adhesive bonding the strength of the interface is lower than the internal strength of the silicone rubber or substrate. Failure of bonding then would occur in the interface.

Usually cohesive bonding is the desired mode meaning the strength of the interface is higher than the internal strength of the silicone rubber or substrate resulting in failure within the rubber or substrate.

The interactions responsible for cohesion and adhesion can be of physical and chemical nature. Bonding interactions of physical origin can be for example physical grafting of linear or branched molecular chains as well as film cohesion due to surface or interface tension. Interdiffusion of polymers in solvents can also contribute to adhesion. Chemical bonding can be either inter or intra-molecular. Intramolecular interactions can be of ionic-metal- and, most important, covalent nature keeping atoms together within molecules, polymers, salts or metals. Intermolecular forces can be either van-der Waals forces like dipole/dipole and dispersion interactions or hydrogen bonding [3]. **Fig. 2** summarizes various contributions to adhesion mechanisms.

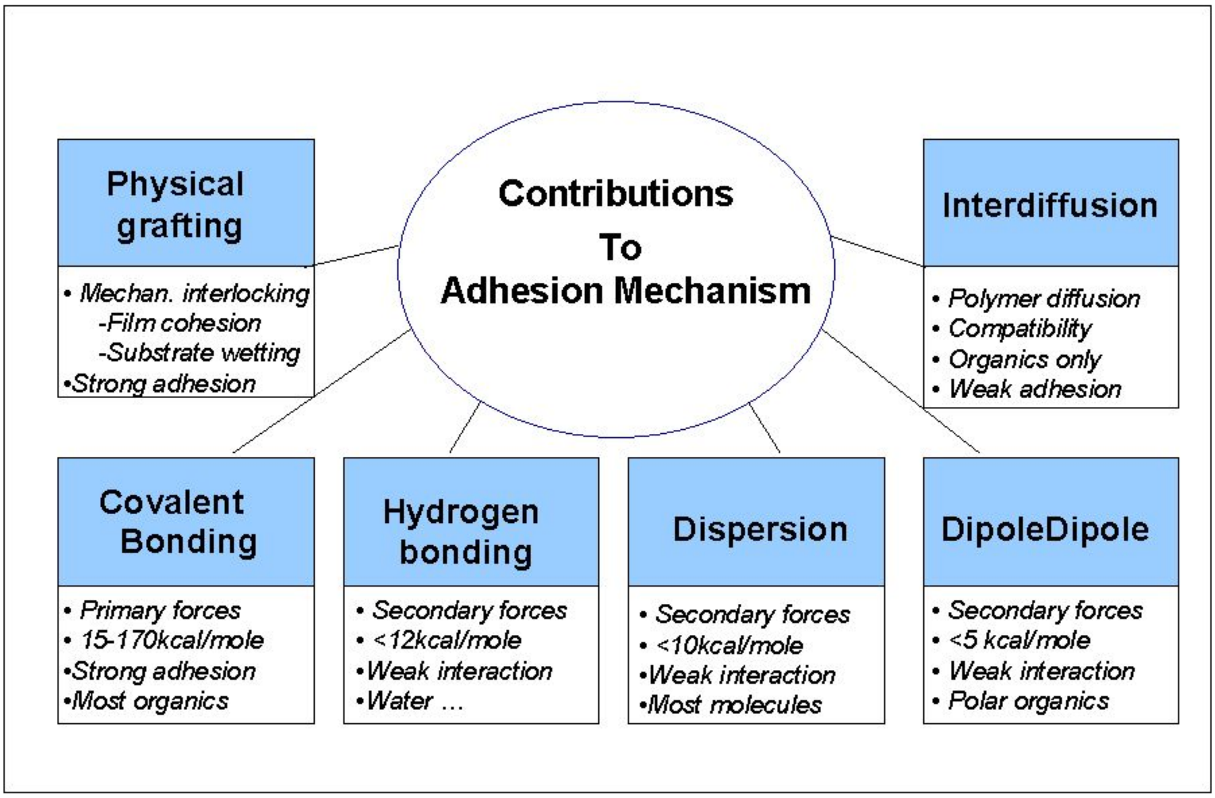

Figure 2: Contributions to Adhesion Mechanism

Bonding Methods

Generally, there are three different technologies that could be used to make a composite combining a rigid component and an elastomeric silicone rubber:

- mechanical combination of the two components by design of the part, reduced flexibility in design and functional integration,
- adhesion by using an external adhesion promoter on the rigid part, requires an additional manufacturing step and handling of solvents and
- adhesion by using an internal adhesion promoter in either the rigid or the flexible component

Mechanical Link

The mechanical combination of two parts e.g. with undercuts or drillings is the traditional method to link a silicone rubber with thermoplastic substrates (**Fig. 3**). With this technology, one can use any kind of Silicone Rubber and a selection of substrates for the composite article. A major disadvantage is that not every plastic part can be designed in such a way that holes or undercuts can be integrated. The mould for the plastic part would also be of a more complex design to get such geometric anchors.

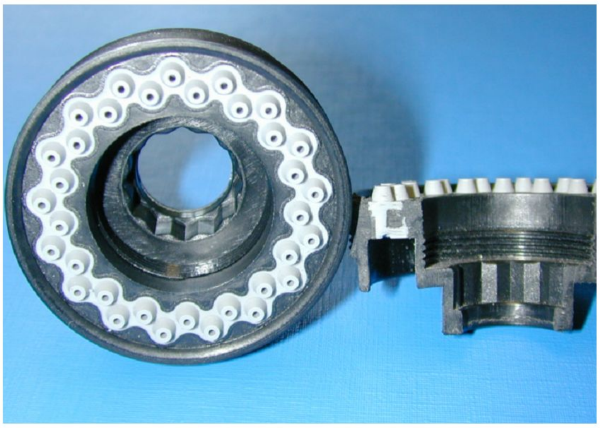

Figure 3: Sample of mechanical link: Showerheads

Primers

A common way to achieve bonding between substrates and silicone rubber is the use of primers. In a process with a primer, the automated processing is normally interrupted. The primer must be applied to the moulded plastic part, usually only to the section of the surface where the silicone rubber will be overmoulded. Then the primer must be activated over time, additional heat or humidity application before the process step may be necessary. With these limitations only few processes can be designed to run 100% automatically.
The major advantage of the primer process is the low cost for smaller series and its exceptional adhesion performance. Special primers are developed to reach excellent bonding of most standard or speciality silicone rubbers to various substrates like engineering plastics, metals, ceramics, glass etc.
A typical example for the application of primers is the production of composite insulators for high voltage applications. Due to the very special requirements on durability, weather resistance and resistance to electrical discharges outstanding bonding between the outer silicone sheath and sheds and the engineering plastic core as well as to various metal fittings is needed. **Fig. 4** shows the finishing of a hollow core insulator produced with Silopren® Electro 242-1 LSR and Primer TP 3790, especially designed for composite insulator application.

Figure 4: Finishing of Composite Insulator

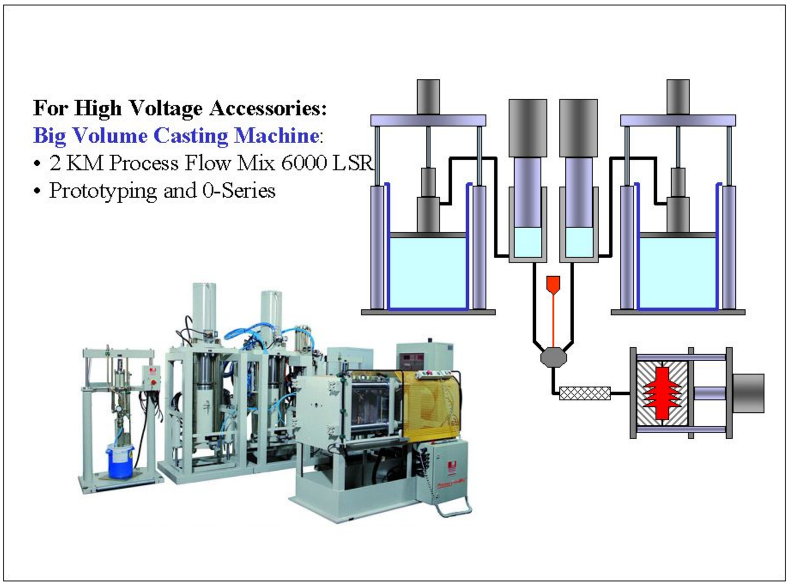

Figure 5: Equipment for High Voltage production

FIG. 5 shows a Big Volume Casting Machine used in the GEBS Application Development Centre for prototyping of high voltage accessories.
To achieve good bonding, the substrate-surfaces usually needs to be pre-treated and degreased e.g. with common solvents, ultrasonic baths with industrial tensides or special treatments like flame, corona or plasma treatments. Usually the primer is applied onto the substrate surface by brushing, dipping or a spraying process. Application of the proper thickness is important here, it can vary from less than 1μm up to 20 μm depending on the nature of the primer. After application and solvent evaporation at room temperature it is recommended for most primers to pre-cure at temperatures between 80 to 130° C for 20 to 60 minutes.
The composition of primers depends very much on the application and of course will not be published by any producer. In general the primer is used to change the surface chemistry and improve the bonding capacity of both partners. Silanols, vinyl groups or even more polar components are used to change the non polar properties of the dimethylsiloxane surface of the silicone rubber. Usually the primers also contain special coupling agents that can be alkoxy-titanium or zirconium based [4] or organofunctional alkoxysilanes or even a combination of both. In the following we will briefly highlight application and chemistry of organo-functional silanes as their utilization increased dramatically within the last 25 years. [5]

Silane Coupling Agents

Silane Coupling Agents are chemicals combining organic and inorganic properties. They are able to react with polymer, mineral or metal components forming durable covalent bonds across the interface. **Fig. 6** describes the anatomy of a typical organofunctional silane.

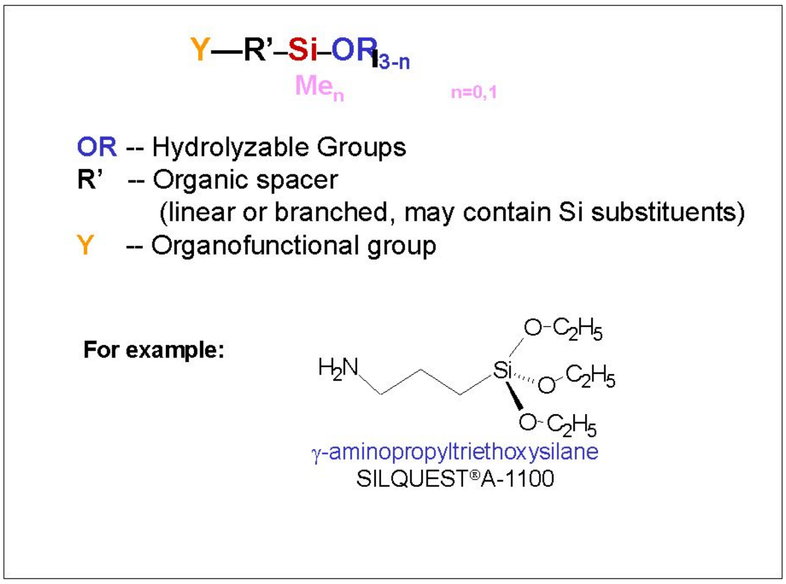

Figure 6: Anatomy of a Typical Organofunctional Silane

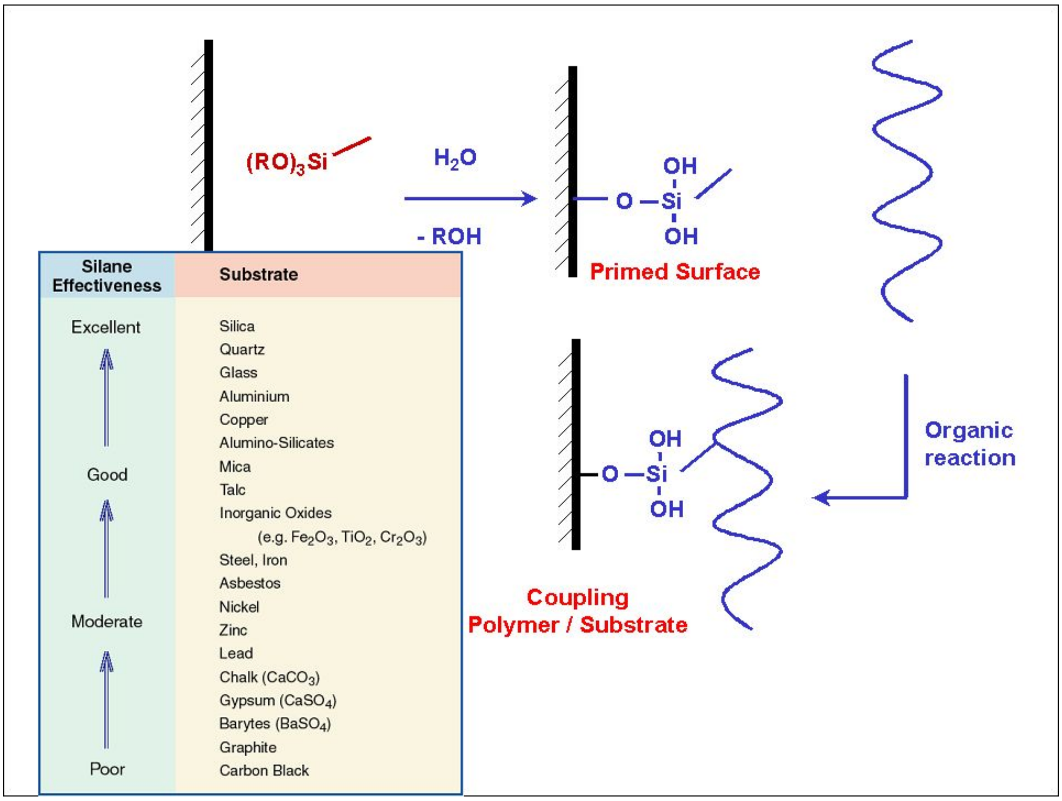

Figure 7: Organofunctional Silanes as Coupling Agents & Primers

OR- is representing an alkoxy moiety, most typically methoxy or ethoxy that can react with various forms of hydroxyl groups generating methanol or ethanol. The resulting silanol groups can provide the linkage with inorganic substrates, fillers or pigments **(Fig 7)** or can undergo condensation reaction with another silanol-group resulting in crosslincking.
Y is usually a nonhydrolyzable organic moiety with organofunctional groups **(Fig 8)** that can react with groups of a coating polymer.

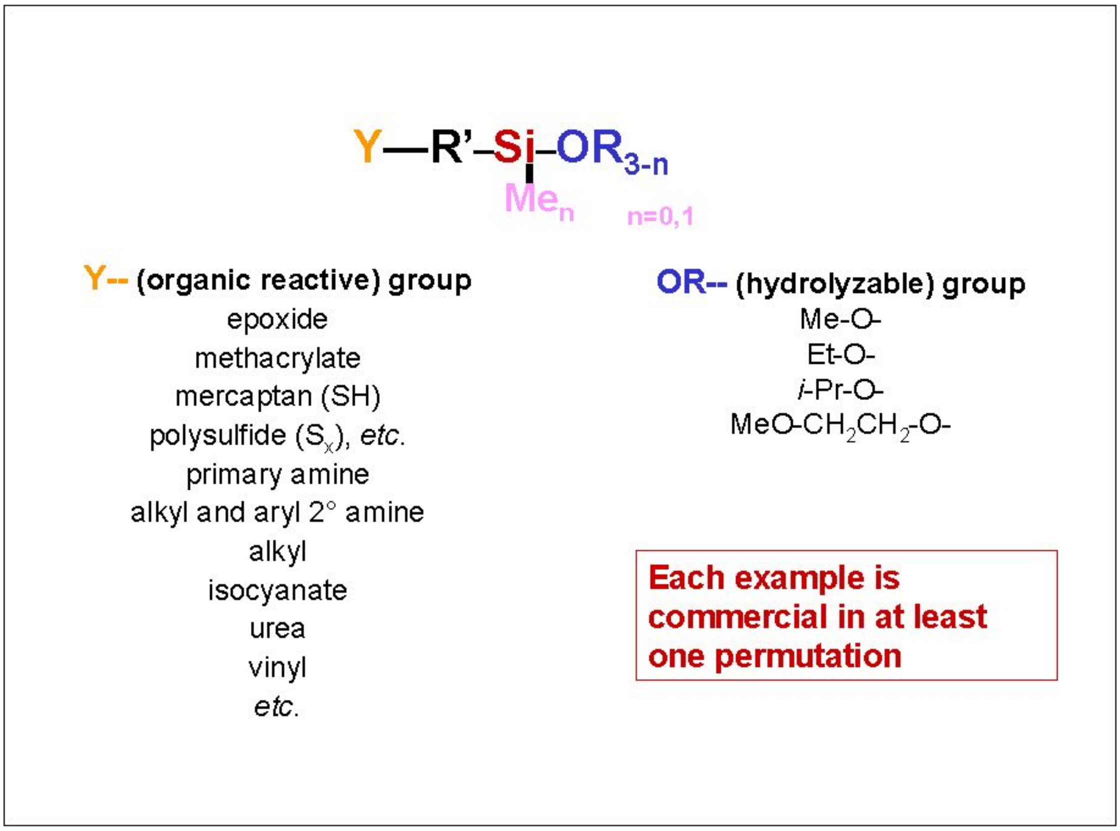

Figure 8: Structures of Organofunctional Silanes

Due to the complexity of silane systems and interactions with various substrates it is extremely difficult to predict exactly, which type of silane provides an optimal combination of properties for a specific system. Several factors like absorption, wetting behaviour, surface energy, acid-base interaction or covalent reaction, to mention just a few, must be considered.

Self Bonding Systems

Recently developed self bonding silicone rubbers show excellent adhesion to a wide range of materials without any treatment of the surface or mechanical links. Typical formulations contain polyorganohydrogensiloxane with a specified SiH content combined with phenyl groups or organosilicon compounds with functional groups e.g. epoxy together with a hydrosilation catalyst [6].
Although we will focus on selfbonding LSR and new processing technology like the 2-component injection moulding process it should be mentioned that also other silicones like HCRs or RTVs can be formulated to be self bonding systems. **Fig. 9** shows various applications of a recently introduced 1-Component-Addition-Cured RTV ranging from cured in place gasket applications to oven door sealings.

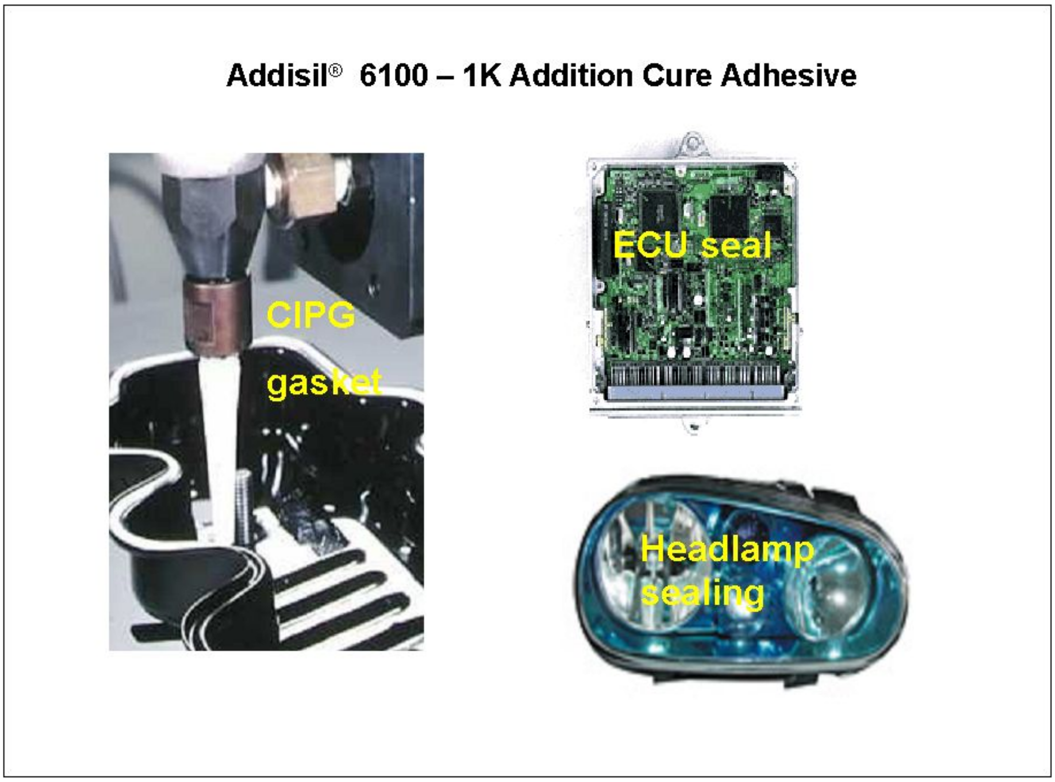

Figure 9: Addisil® 6100 applications

Selfbonding Liquid Silicone Rubber

Using the new generation of selfbonding LSR first of all allows a fast 100% automated cycle. The rigid part can be designed without undercuts or drillings resulting in a more simple mould design. The new generation of self-bonding Liquid Silicone Rubber **Fig. 10** also shows good bonding to inserts like steel or aluminum without mould cavity treatment with a release coating.

Test of Properties

To test the bonding properties between selfbonding LSR and substrate a special peeling force test is used. **(Fig.11)** shows the force required to separate Silopren® LSR 27xx and various substrates. The test articles are made in a 2-component injection moulding process. The adhesion between the selfbonding Liquid Silicone Rubber and the substrate increases after moulding. A fresh moulded part has normally a lower peeling force value than one tested some days later. This effect can also be accelerated by post curing the finished articles.

Grade	Silopren LSR/LIM Type	Shore A/ Others
Technical	LSR 2730	30
applicat-ions	LSR 2740	40
	LSR 2750	50
	LSR 2760	60
Strengthend adhesion	LIM 8040	40
reqires Mold coating	LIM 9040	40 Low Comp. Set
Self Bleeding	LSR 2735/30	30 3 % oil content
	LSR 2715/50	50 1 % oil content
BgVV/FDA confirm	LSR 2752	50

Figure 10: **Selfbonding LSR Grades**

Substrate	Peeling Force DIN 53 289
PA 12	2,5 N/mm
PA 6	4,5 N/mm
PA 6.6	5,0 N/mm
PBT	5,3 N/mm
PPE	4,0 N/mm
PPS	2,5 N/mm
PPA	3,9 N/mm
PPE/PA	2,7 N/mm

Figure 11**: Adhesion of Silopren®LSR 27xx to various substrates**

Processing of LSR

Processing of Liquid Silicone Rubber can be done in injection moulding machines with some extra features required for the handling of this material. For this a pump feeds the viscous two-component material through a static mixer in a special, cooled injection unit where it is injected into a heated mould (150 -220°C). Depending on the geometry of the part, the Liquid Silicone Rubber cures in a short time and the article can be demoulded easily.

2-Component Injection Moulding process

Various processes are developed nowadays for moulding articles of 2-Component Rubers **(Fig12).**

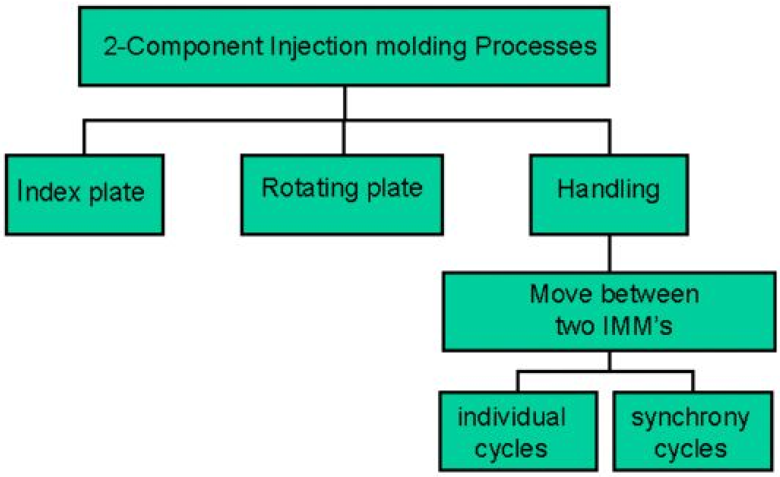

Figure 12: Overview 2-Component Injection Moulding

Insert Technology

A frequently employed process for 2-Component Injection Moulding is the insert technology. The rigid part has to be moulded in a first step. The moulded engineering plastic (ETP) can be placed into the Liquid Silicone Rubber mould by hand or in an automated process by a robot – depending on the production quantities and processing cost. **(Fig. 13)**

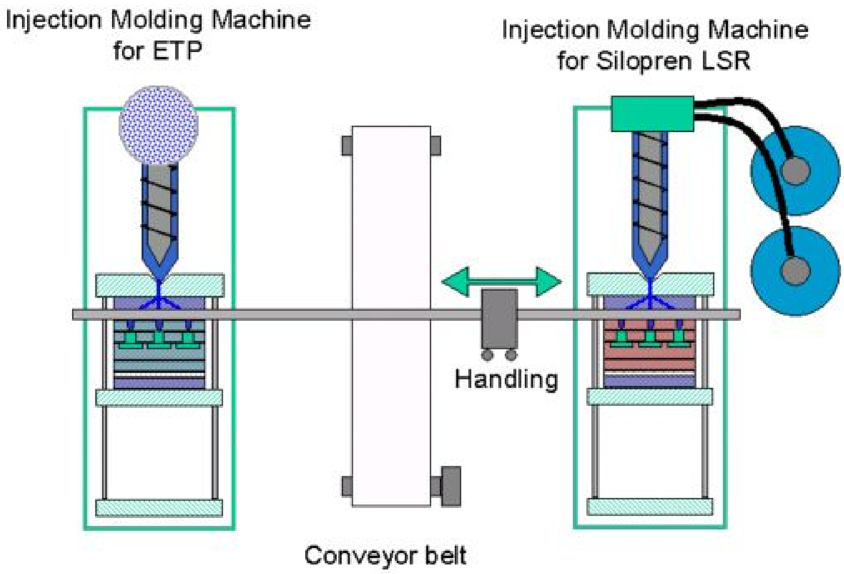

Figure 13: Conventional Insert Technology with Handling

In this process the advantages are that the producer has 2 independent injection moulding machines that could be used for other projects as well. If required, an extra surface treatment can be applied to the rigid part before overmolding with LSR.

2-Component Injection Moulding machine

Different technologies are possible when moulding on a single machine. Often the ejector side of the mould rotates in the process by 180°. With this the just moulded rigid part is placed into the cavity where the Liquid Silicone Rubber will be over-moulded. **(Fig. 14 A)**

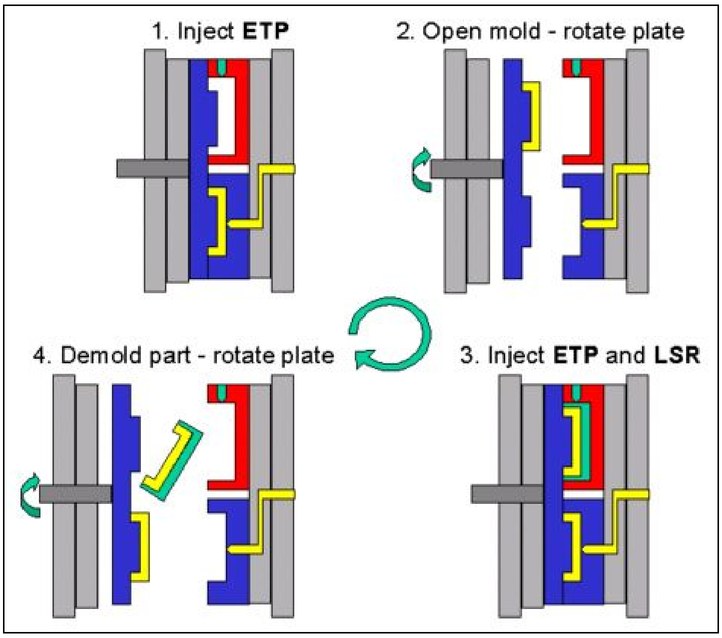

Figure 14A: *2-Component Injection Moulding machine with rotating plate*

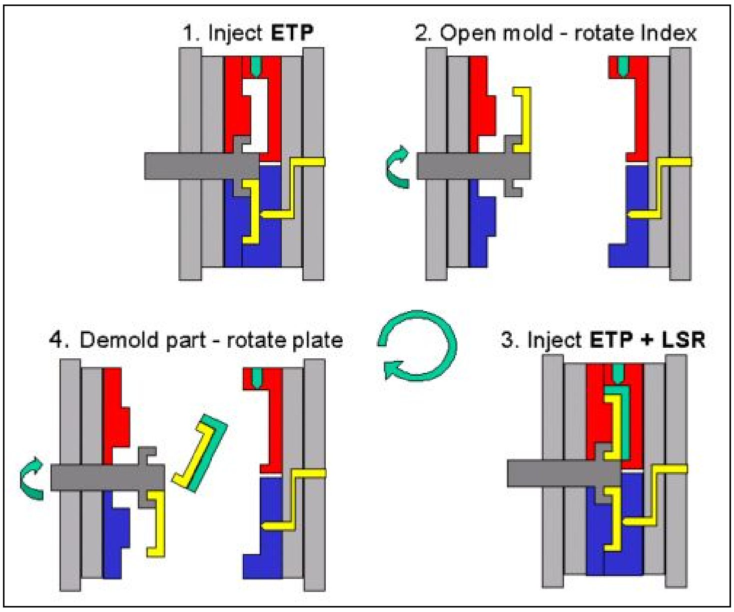

Figure 14 B: 2-Component Injection Moulding machine with index plate

In some cases it is advantageous not to rotate the whole ejector side but only an index plate. **(Fig. 14 B)**
In these two technologies the difference lies in the temperature distribution over the mould cross-section. Using the rotating plate the ejector side has an equal temperature, depending on the temperature required for the

plastic part. Compared to this the index plate rotates the plastic article in a cavity that is heated up to the preferred curing temperature of the Liquid Silicone Rubber.
The temperature used in the process mainly depends on the temperature resistance of the plastic. For this reason engineering plastics like PA, PBT, PPA or PPS are preferred as a combination partner for the Liquid Silicone Rubber.

Conclusion

The main intention of this revue is to provide a brief update on innovative solutions for the design of composites comprising silicone and rigid materials. Of course only a few examples out of a multitude of possible applications could be given. Important contributions like surface treatment were only briefly mentioned. The vast amount of substrates as well as countless coupling agents - 8000 new patents containing the key words “silane” and “coupling agent” granted within the last 30 years [5] – requires extensive application testing. Bonding to “difficult” substrates like polycarbonate or polypropylene remains challenging.
The application developer should also keep in mind that even small variations of chemistry/additives and/or surface of each substrate can change the adhesion to the silicone rubber significantly. Therefore a close cooperation of all partners including material suppliers already in the early state of any project is highly recommended.

[1] N.N., *Silicones – Chemistry and Technology*, Vulkan Verlag, Essen, **1991**
[2] W. Noll, *Chemie und Technologie der Silicone*, Verlag Chemie, Weinheim, **1968**
[3] G. Habenicht, *Kleben- Grundlagen-Technologie-Anwendungen*, 2. Auflage, Springer **1990**
[4] P.J. Moles, *J. Adhesion Sci. Technol*. Vol. 6 No 1. pp 61-71 **1992**
[5] M.J. Moore, *ACS Rubber Division, 160th Fall meeting*, 16.-19.10.**2001**, Clevleand, Ohio,
[6] EP 0686671, EP 1106662, DE 10204893