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## Adhesion

## Wetting

Wetting is involved when a solid and a liquid makes contact. Different fluids have different wetting, for example: if you wash your hands with water it spreads and “wets” the skin. If you would break an old barometer or mercury thermometer and get mercury on your hands it would not flow over your skin but it wouldn’t wet your skin because the mercury would just roll off your hand. The difference why one fluid wets and the other doesn’t can be explained with the contact angle. The contact angle (θ) can range in between 0˚ and 180˚. If the contact angle is above 90˚ it means that the wetting of the surface is favorable and the fluid will spread over the surface. A contact angle higher than 90˚ generally means that the wetting of the surface is unfavorable so the fluid will minimize the contact with the surface and form a compact droplet. A contact angle of 0˚, which is an extreme case, means that the degree of wetting is perfect and the fluid spreads out on the surface becoming a thin film, an example of perfect wetting is oil being poured on a steel sheet. The other extreme is a contact angle of 180˚, which is called non-wetting and this cannot exist for a solid/liquid interaction. The difference between hydrophobic (low wetting) and hydrophilic (high wetting) surfaces can be seen in figure 1.

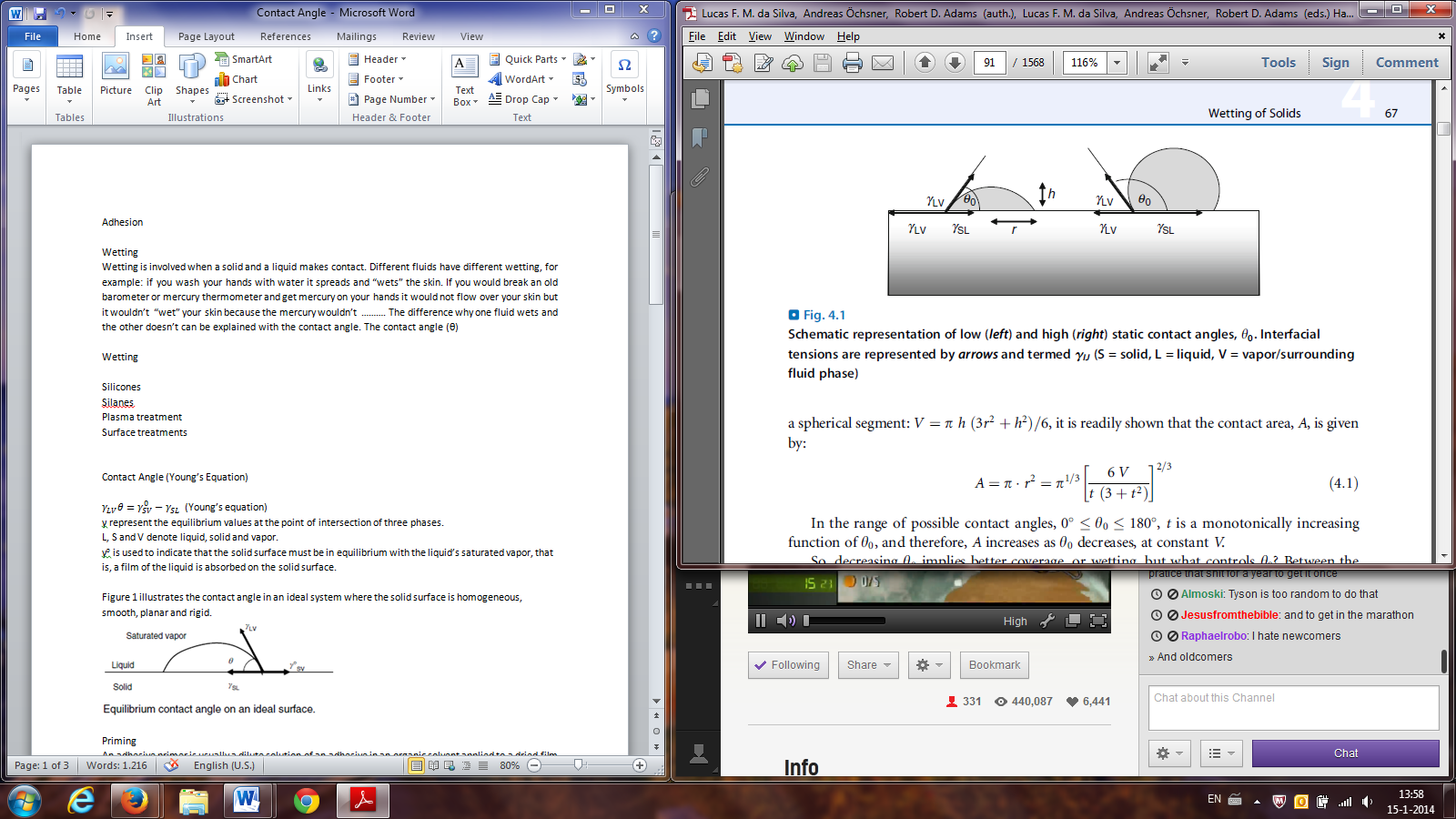


Figure : An example of a low and high contact angle. Interfacial tensions are shown by arrows and termed ϒ (L = liquid, S = solid, V = vapor/surrounding fluid phase)

The third phase that can be seen in figure 1 is the gas phase. The measurement is done where the three phases meet, the surrounding medium is regarded as air, but more precisely; the surrounding area of the droplet always contains vapor of the liquid and in very few cases, that of the solid too. The interaction between the liquid and the gas phase are important and have to be taken in the calculations to get a contact angle.

A way to calculate the contact angle can be done with the Young equation (1), whereas the ϒsg stands for the solid-vapor interfacial energy, ϒsl as the solid-liquid interfacial energy and ϒlg for the liquid-vapor interfacial energy. This equation does assume that the surface is flat and rigid.

## Silicones

Hechtingverbeteraars worden al gebruikt etc.

### 3.1 General information

Silicones are built from siloxanes which are polymerized together and are called polysiloxanes. The common formula for polysiloxanes is [R2SiO]n. The materials exist of an inorganic silicon-oxygen backbone […-Si-O-Si-O-…] with side groups attached to the silicon atoms. These side groups can be an organic group like methyl, ethyl or phenyl but an inorganic material is also possible. The side groups can be linked to another chain, causing crosslinking. By doing crosslinking, using different side groups an varying the backbone lengths, silicones can be synthesized with a wide variety of components and properties varying in temperature, viscosity, tensile strength and many other properties. Silicones themselves already have a low thermal conductivity, low, low toxicity, chemical reactivity and in general thermal stable, which makes it a good substance for multiple applications. Furthermore it is resistant to oxygen, ozone and UV light.

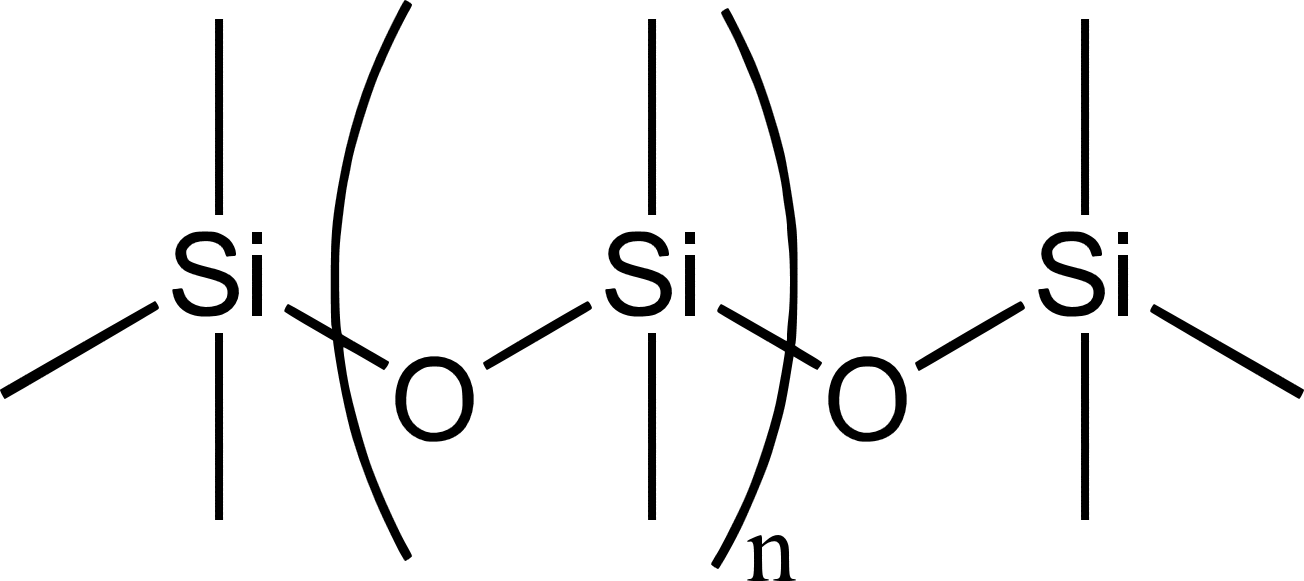


Figure 2: General structure of silicones

### 3.2 Synthesis of silicone

Basic silicone polymers are obtained by a three-step synthesis.

1. Chlorosilane synthesis

Reduction of quartz at high temperature so that Silicon metal can be obtained (1) and by using it with methylchloride, dimethyldichlorosilane can be obtained (2). This will be the monomer for the preparation of polydimethylsiloxane (PDMS), the chlorine groups can be replaced by alcoholysis. In this way various silanes with different functionalities can be prepared.

(1)

(2)

1. Chlorosilane hydrolysis

PDMS are obtained by the hydrolysis of the dimethelychlorosilane in presecence of an excess of water which gives a reaction that gives a mixture of linear and cyclic oligomers (3).

(3)

### 3.3 Polymerisation, polycondensation and crosslinking

The oligomers gotten out of the hydrolysis of dimethyldichlorosilane have too short chains for most applications. To make them longer they need to be condensed (linears) or polymerized (cyclics). For opening the cyclics to make linear chains can be catalysed with a lot of acid or base compounds. This will give an equilibrium mixture with cyclic oligomers and polymers. The size of cyclics depends on the substituents along the chain, pressure and temperature of the solvent. The chain length of the polymers depends on the presence of substances capable of giving chain ends. The functionality of these ends will depend on the presence of end-blocking agents. Linear condensation is an equilibrium reaction catalysed by acids or bases.



The silicone polymers are easily transformed into a three dimensional network and an elastomer by a crosslinking reaction, which allows the formation of chemical bonds between chains. Crosslinking can be done by condensation, addition or radical reaction. Since condensation

## Surface treatments

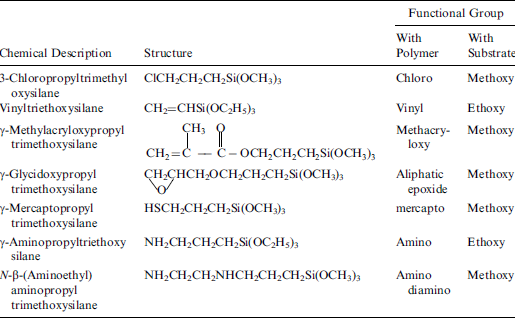
## Silanes

Silanes are commonly used to improve the adhesion in sealants. Silanes of the general structure (R-Si(OR’)3, where R is an organofunctional group and R’ a hydrolysable group, constitute of one of the most important group of adhesion promoters used these days. Silane molecules are bifunctional, containing an organofunctional group that can react with polymers and polar silanol groups. The basic reaction of silane coupling is found in figure x. The easiest way to let the reaction done is lowering the pH with an acid.

http://puu.sh/7rcFw.png

To apply a silane on a surface, the surface must first be cleaned, then the silane needs to be dissolved into water with a few droplets of an acid to decrease the pH. Apply it with a cloth and wipe it in and then it needs a couple of hours of drying to let the silane bind with the surface. The primary target is to increase the number of bindings possible on the surface.

Various silane adhesion promoters can be found on the market and are all different from each other, a few of those can be found in table x.



These are however not all usable for silicones. The silanes that have been used before in other experiments done by other researchers are methylacryloxypropyltrimethoxysilane, glycidoxypropyltrimethoxysilane and aminopropyltriethoxysilane.

#### 4.1 Plasma treatment

Plasma treatments can be done with Ar, O, He or N2 to cross-link, etch and activate different sorts of polymers like PET, PC and PMMA. Depending on the gas composition and plasma conditions, electrons, ions, radicals, fast neutrals and VUV (vacuum ultraviolet) radiation contribute to the treatment of the polymer, resulting in etching activation and/or cross-linking [source]. A plasma treatment can also have negative effects on the polymer surface, causing degradation when it is exposed to plasma for a longer period of time or a too high intensity. The reason that it happens is that the polymer is interacting too much with the radicals or ions.

A research done in 2003 (D. Hegemann et al)[source] tested multiple polymer foils (PET, PMMA, PC, PC/ABS, PP, PS PE and EPDM) with plasma treatments at different variables to look at the etching, wetting and adhesion improvement and friction reduction. In figure [x] the found results of the conducted experiments can be found back and it can be seen that SiOx and N2 make the surface hydrophilic, increasing the wetting overall on the surface of PC. [11, D Hegemann; plasmas polymer 6 2001].

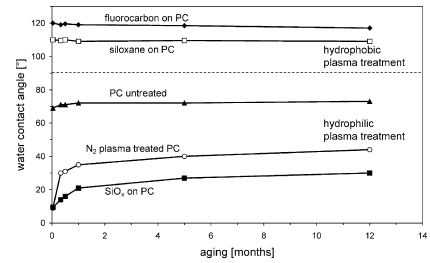


Figure : Aging of untreated, plasma treated and coated PC sheets

There are a lot of different ways plasma can interact with the polymer surface. The gas type and plasma conditions can be varied to minimize the degradation and aging effects of the polymer type like PC and EPDM. Plasma treatments can improve wetting and friction properties of polymers by treating the polymer once.

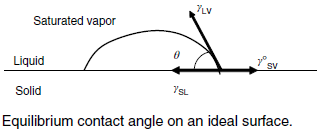
Possible to do on PET, only needs a total of 8-10 seconds to increase the adhesion/surface energy. Done with a plasma treatment device that does it for 5 minutes (300 seconds) with Nitrogen.

Contact Angle (Young’s Equation)

(Young’s equation)

γ represent the equilibrium values at the point of intersection of three phases.  
L, S and V denote liquid, solid and vapor. γ0 is used to indicate that the solid surface must be in equilibrium with the liquid’s saturated vapor, that is, a film of the liquid is absorbed on the solid surface.

Figure 1 illustrates the contact angle in an ideal system where the solid surface is homogeneous, smooth, planar and rigid.



Priming

An adhesive primer is usually a dilute solution of an adhesive in an organic solvent applied to a dried film with a thickness of 0.0015-0.05 mm. Some of its functions include

* Improved wetting
* Protection of the adherend surface from oxidation after surface cleaning
* Inhibition of corrosion

An important difference between metals and plastics is in their surface energy. Polymers have inherently lower surface energy than metals (assuming they are contamination-free) and tend to form intrinsically poor adhesion bonds without some type of treatment.

(Ebnesajjad, S. and C.F. Ebnesajjad, Surface Preparation Techniques for Adhesive Bonding , William Andrew Publishing/Noyes, Norwich, NY, 2006)

Plasma treatment

Possible to do on PET, only needs a total of 8-10 seconds to increase the adhesion/surface energy.

Page 118 – 120 adhesives technology handbook 2nd edition

Handbook of Adhesion Technology (da Silva, Öchsner, D. Adams)

The Si–O bond is stronger and more flexible than the C–C or the C=C bond. Thus, silicon polymers are physically stronger and more flexible than typical organic polymers. Furthermore, silicone possesses rubber elasticity due to its organic functionality allowing limited cross-linking between polymer chains.

Recent research activity into peel testing (Kinloch and Williams 2002) has thus focused on the development of procedures (both test techniques and analysis schemes) to isolate the energy required to fracture the peel sample, termed the adhesive fracture energy, GA, from the total input energy to the system, termed G. The underlying energy balance is:

GA ¼ G Gp; ð20:28Þ

where Gp represents the plastic energy dissipated in the peel arm. In, for example, the 90 fixedarm peel test for flexible to rigid peel arms, energy is dissipated by local plastic bending of the peel arm at the peel front.

The chemical structure of silicon is different from that of carbon-backbone-based (organic) polymers with C–C repeat units. Specifically, the polymer chain backbone consists of repeat units. The Si–O bond is stronger and more flexible than the C–C or the C=C bond. Thus, silicon polymers are physically stronger and more flexible than typical organic polymers. Furthermore, silicone possesses rubber elasticity due to its organic functionality allowing limited cross-linking between polymer chains.

Silicone Chemistry and Properties

Most commercial silicones are made from a chloro-alkyl, a silicon-metal, and a catalyst and/or pressure. This reaction produces low molecular weight silanes and linear and cyclic siloxane as intermediates products. Silanes are widely used as adhesion promoters in organic and inorganic polymers, adhesion primers, coupling agents for custom reaction syntheses, and coupling agents to promote bonding of fillers to polymer matrices in composite materials. Silicones are typically formulated to provide a three-dimensional network of siloxane. Hydrocarbon radicals such as methyl, phenyl, vinyl, fluoro, amino, hydroxy, ethoxy, and other organic groups are attached to the silicon atom under heat, frequently combined with the action of metal catalysts, such as tin or platinum compounds, to condense the polymer into a rigid thermoset material. Use of functional vinyl improves compression set resistance and provides higher cross-linking density. Use of functional fluoro increases chemical and ozone resistance and provides higher temperature resistance. It also decreases polymer opacity by preventing haze-causing crystallinity with increased steric hindrance along the polymer chains. Silicon can also be synthetically polymerized with starting materials of quartz (sand) and chlorine and an organometallic reagent. Silicons have excellent thermal and oxidative stability at high temperatures, up to 260C and remain flexible at temperatures down to -75C. They possess excellent electrical properties, including resistance to corono breakdown. They exhibit general inertness, exhibited as resistance to weathering, ozone, and many chemicals and also exhibit general non-corrosiveness to other materials, with the exception of some construction adhesives in contact with ferrous alloys in closed, moist environments. They are inherently nonflammable and have self-extinguishing properties. Silicones exhibit lubricity and other unusual surface properties, such as low surface tension of the fluid resin, and the capability of preventing other materials from sticking, as well as very low water absorption. Even though its tensile strength is lower than most organic rubbers at room temperature, silicon rubber has higher tensile strength than most organic polymers at 204C.

Silicone Product Forms and Applications

Silicon fluids: Methylsilicone fluid is the most common product, with relatively constant viscosity over a range of temperatures and it exhibits shear stability with high pumping pressure. Industrial applications of silicon fluids include uses in fermentation adhesives, and sealant manufacturing. Room temperature vulcanizing (RTV) type: RTVsilicon rubbers are used as one- and two-part adhesives and sealants. Applications include bonding ofmetals, polymers, and ceramic substrates, as well as formation of sealant barriers against liquids and certain vapors. RTV rubber cures by either a condensation or an addition reaction. In the condensation cure, the basic polymer is a silicon fluid in either one-part or two-part form. Vulcanization chemistry of RTV materials must be kept in mind during material selection since some condensation cure reactions release acetic acid and ammonia vapors which can be corrosive. Alternatively, natural-curing RTV materials are availablewith alcohol, oxime, platinum, and tin vulcanizate reactions. Rheologically, RTV materials range from a flowable, pourable consistency to the thixotropic paste form. One-part type: For one-part-type silicones, both the catalyst and the cross-linking agent are incorporated in the base compound at the time of manufacture, which involves compounding a silanol-stopped silicone polymer with an excess of cross-linker. The one component silicones typically cure with moisture. Exposure to atmospheric moisture causes further curing of the silicone rubber to take place. Diffusion of moisture into the rubber progresses vulcanization from the surface inward. One-part component type silicones are excellent adhesive sealants and can be formed in place as gaskets. They can also be used to form films by solvent dispersion.

Two-part type: As for one-part-type silicones, both the catalyst and the cross-linking agent are incorporated in the base compound just before use. They are generally silanol polymers, cross-linked with alkoxy silane or oligomers and organic tin compound catalyst. Two-part-component-type silicones are typically used for applications in coatings, adhesives, and encapsulants. Heat-curable rubber (HeR): These are typically silicon rubber compounded with catalyst, color, and additives mixed and milled into siloxane polymers. HCRs are often used in molded parts for high-temperature service or in applications that utilize their chemical and weathering resistance, but also see applications as seals and gaskets.