

Review

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## Surface pretreatments for medical application of adhesion

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### Abstract

Medical implants and prostheses (artificial hips, tendon- and ligament plasties) usually are multi-component systems that may be machined from one of three material classes: metals, plastics and ceramics. Typically, the body-sided bonding element is bone.

The purpose of this contribution is to describe developments carried out to optimize the techniques, connecting prosthesis to bone, to be joined by an adhesive bone cement at their interface. Although bonding of organic polymers to inorganic or organic surfaces and to bone has a long history, there remains a serious obstacle in realizing *long-term* high-bonding strengths in the *in vivo* body environment of ever present high humidity.

Therefore, different pretreatments, individually adapted to the actual combination of materials, are needed to assure long term adhesive strength and stability against hydrolysis. This pretreatment for metal alloys may be silica layering; for PE-plastics, a specific plasma activation; and for bone, amphiphilic layering systems such that the hydrophilic properties of bone become better adapted to the hydrophobic properties of the bone cement. Amphiphilic layering systems are related to those developed in dentistry for dentine bonding.

Specific pretreatment can significantly increase bond strengths, particularly after long term immersion in water under conditions similar to those in the human body. The bond strength between bone and plastic for example can be increased by a factor approaching 50 (peeling work increasing from 30 N/m to 1500 N/m).

This review article summarizes the multi-disciplined subject of adhesion and adhesives, considering the technology involved in the formation and mechanical performance of adhesives joints inside the human body.

### Introduction

Implants and prostheses can help provide numerous useful functions for the human body. However, a device fabricated from a single material usually cannot meet all

physical requirements for successful implantation and function. Therefore, implants and prostheses usually consist of composites and mixtures or alloys.

Over the last decade, the growth in the use of adhesives for medical applications has been rapid, with many important developments in the technology of adhesive techniques being reported. This growth has also drawn attention to basic studies in the science of adhesion and adhesives, particularly concerning stability under wet conditions. There are many analogies between adhesive bonds for industrial applications and the requirements for pre-treatments and adhesives inside the human body. For many industrial applications, stable bond strengths are mandatory, particularly in the presence of elevated temperature and humidity. These conditions are also present in the human body. In common for the human body and many industrial applications is the relative humidity of 100%, a challenge for any adhesive joining. The elevated temperature (37°C inside the body compared with room temperature) means higher diffusion rates of water molecules through permeable materials like plastics [1].

Long-term stability is crucial for attaining a useful service-life. A bonded component may deteriorate upon exposure of the adhesive interface to its normal operating environment. In the case of structural adhesive interfaces consisting of metallic substrates, empirical investigations established many years ago revealed that water, either in liquid or vapor form, is the most hostile environment that is commonly encountered. The presence of moisture, rather than other components of body fluids, is responsible for the environmental attack, while an applied mechanical load further increases the rate of adhesion loss. The loss in strength is attributed to the de-bonding of resin from the metal by the intrusion of water, since obviously the interface between such dissimilar materials as an organic polymer and a metal does not allow the formation of a water-resistant bond. Similar reasoning holds that a similar effect occurs when the substrate is a ceramic or a plastic. Here, also, the presence of water is the most hostile environment when its molecules come into competition with the bonds between the adhesive and the prosthesis. Thus, suitable technologies need to be developed to join different compound materials adhesively to each other or to human body structures when long service life with sufficient adhesion strengths is the goal. For implants and prostheses, long-term stability means a low failure rate over the total implant time.

In the following review, some issues from the medical fields for which adhesive techniques are already established or for which the functionality may be improved by adhesive techniques are discussed, particularly within the background of our research results.

## Review

### **Orthopedic total endoprostheses**

Hip replacement surgery in the developed countries is becoming more common as the population has increasing life expectancy. There are two types of artificial hip replacements, the cemented prosthesis focused in the present investigation, and the uncemented prosthesis, which is not being considered here.

Each prosthesis is made up of two parts, the femoral stem component which replaces the femoral head and neck, and the acetabular cup component which replaces the acetabulum. Both are held in place by polymethylmethacrylate (PMMA) using cementing fixation technique. The femoral stem is made of metal (CoCr- or Ti-alloy) and has a modular ceramic ball on its neck that fits into the acetabular cup component and acts as a low friction bearing. The acetabular cup is most frequently made out of ultra-high molecular weight polyethylene (UHMWPE).

There are many reasons why an artificial hip replacement finally fails [2]. Aseptic loosening of cemented implants causes more than 80% of clinical revisions [3–5]. Although this loosening may be due to a wide range of different factors, several researchers having performed clinical and histological studies have been able to show that the beginning of the aseptic loosening process in femoral stems is found in the cement-metal interface (debonding) [6,7]. Supported by diffusion and capillary forces, water molecules find their way into the bone cement and finally into the bone cement-metal interface, separating cement from metal by hydrolytic degradation of the primary bond.

As a consequence of the de-bonding, micro-movement between the implant and bone cement starts and then increases, and eventually leads to the development of wear debris of cement particles, cement fissures, and cement fractures, with the formation of osteolytic reactions within the periprosthetic bone. Loosening of the prosthesis is the final result [8].

Although the rate of loosening has been reduced over the past two decades by improved cementing technology and more suitable implant materials, permanent resistance to hydrolytic degradation of the bond of the acrylic PMMA onto the metal surface remains an important unsolved problem in total hip arthroplasty of the femoral stem. In contrast, the weak link of the chain of bonding on the acetabular side is the long-term bond stability between the acrylic PMMA and the acetabular bone stock. There is no true microinterlocking between the cement and the subchondral sclerotic acetabular bone after reaming the acetabulum. Several studies of primary total hip arthroplasties with cemented cups showed an increasing failure

rate after 8 to 10 years of implantation. On the acetabular side, the bond between the polymer polyethylene and the polymer bone cement is not of primary concern in reducing the rate of loosening, nevertheless it should not be forgotten.

In this review, the metal stem and the plastic acetabular cup will be the main focus for applicability and usefulness of adhesion techniques with the aim of reducing the described deficiencies

#### Metal femoral stem

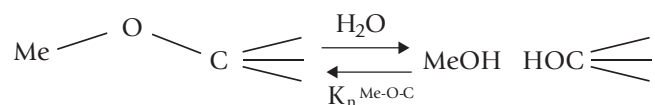
##### Basics

The metal femoral stem is implanted into the femur after the bone has been prepared by rasping within it a conical cavity. No adhesive is needed when the implant is fixated without cement ("uncemented prosthesis"), since the implant surface is covered with a fine mesh of holes (e.g.) that allows bone to grow into the mesh and to tightly attach to the prosthesis. However, an adhesive technique becomes necessary when the prosthesis is to be held in place by bone cement ("cemented prosthesis"). Bone cement has a methacrylate base, and is used to glue the metal shaft to the mostly cancellous bone of the femur cavity walls (exception: in a hip re-operation, the walls are no longer cancellous). The interfaces metal stem/bone of the femur are mechanically (walking, jumping, etc.) and chemically (body reaction, temperature, humidity) stressed. Whereas the cancellous bone offers many retentive centers that facilitate a long-life effective anchorage of the bone cement to the inner walls of the cavity, the metal surface, however, is much more subject to the risk of debonding. Since the surface of the metallic femur (usually machined out of CoCrMo or TiAl6V4 alloy) is substantially smooth, mechanical retention has secondary meaning and chemical bonding is essential [9,10]. Even if there were mechanical interlocking, experience has shown that with the moist conditions of the human body, interlocking between a plastic and a metal alone is not sufficient for a stable bond [11–13].

Water, omnipresent in the body, has an aggressive impact on the metal/acrylic joint interface, in particular because of the strong dipole moments of the water molecules. The interface is not protected against the attack of water even if a gap-free and tight contact between substrate and adhesive could be established. The water molecules can penetrate into the interface by diffusion, since the bone cement as a plastic is permeable; the water molecules are responsible for the hydrolytic load of chemical bonding of any kind. Water molecules diffuse through any acrylic polymer, and eventually reach that interface which is expected to guarantee the bond between the two materials. Individual water molecules become clustered into a liquid phase. The chemical bond strength is then challenged. The dan-

ger of water at the interface is primarily not determined by the rate of permeation of water through the polymer matrix, but by the amount of moisture finally retained at the interface.

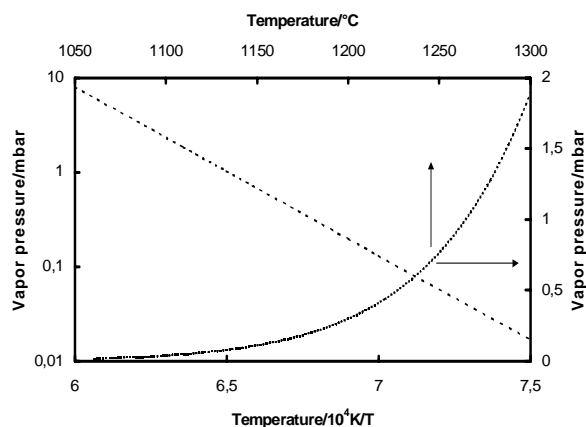
Metal surfaces form metal-oxides, oxide-hydrates, and hydroxides when they are exposed to a moist, oxygen containing environment. Therefore, after application the PMMA bone cement does not come in touch directly with the atoms of the bare metal surface, but rather with the metal-oxide layer on it. Such oxide layers may allow high initial bond strengths to an acrylic polymer because of bridge linkage, dipole-dipole interactions, and polarization effects. These high initial bond strengths, however, decrease under the influence of clustered water molecules, which shift the chemical balance that is inside the layer system responsible for bonding, towards the hydrolyzed state of the interface. The chemical balance, although highly simplified, can be illustrated as follows:



C stands for a carbon atom of the PMMA. After decomposition involving splitting of bonds and addition of the elements of water, the bonding strength decreases because the *hydrolyzed* links (right handed side) can only bear fewer mechanical stresses [14].

The water molecules penetrating the PMMA, however, do not only have deteriorating influences, but also healing effects. The interface becomes pre-loaded during polymerization [15], and the corresponding shrinkage stresses the interface mechanically. This shrinkage is partly compensated by the materials' expansion due to penetrating water. This expansion (1–2%) in part releases the stress due to post polymerization shrinkage (6–7%).

The use of a silane [28] as a bonding agent does not solve the problem of unstable bond strength, since the covalent bonds between a silane and the hydroxyl groups -OH of a metal surface have too poor a hydrolytic stability as well. The silane can realize chemical bondings to the CH<sub>2</sub> groups of the methylmethacrylate [16–19], but not to the metal, since silane coupling agents are designed to stick to *mineral* surfaces by siloxane bonds, while a metal surface, even if oxidized, does not have the active groups that are needed. In the presence of a wet atmosphere, the silane coupling agent is not efficient in contact with a bare metal oxide without mineral enrichment, and hence it is not able to stabilize the bonding when high long-term bond strength is required.

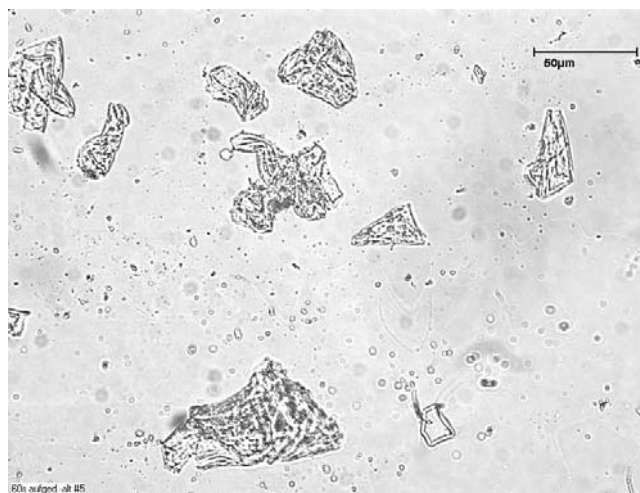


**Figure 1**

Vapor pressure of silicon monoxide vs. temperature on linear (on the right) and logarithmic scale (on the left).

Hence, it becomes obvious that the long-term adhesive strength between silane interlayer/methylmethacrylate and the metal surface can be improved only if the metal surface is modified by an adequate mineral coating [16,20,21]. To this end, an additional interlayer of silica is added such that silicon oxide ( $\text{SiO}_x$ ) is adhered to the oxides already present on the metal surface [22–24].

Silicon monoxide is evaporated in a high vacuum atmosphere ( $p \approx 0.8 \dots 3 \cdot 10^{-5}$  mbar) by resistance heating of an evaporation boat loaded with granulated silicon monoxide. The inner part of the boat has three compartments. Two baskets on either end are filled with silicon monoxide granulate. Above the central basket, which is empty, there is a round chimney through which the vapor stream passes. A baffle extending down from the cover completely surrounds each basket. In addition to the baffles around the baskets containing the silicon monoxide, the cover has a lip that fits snugly and overhangs the boat on both sides. The ends are sealed as the cover and evaporation chamber clamp together to form the electrical terminations of the evaporator. Thermal shielding surrounds the evaporator and is attached so that the shields do not produce undesirable cold spots in the evaporation chambers. After loading with about 3 g of silicon monoxide, the chamber is electrically heated to  $1150 \pm 2^\circ\text{C}$ . The temperature is measured by means of a thermocouple that is mounted in one of the baskets that is filled with the silicon monoxide. At this temperature, silicon monoxide has a vapor pressure of about  $10^{-2}$  mbar (Fig. 1), note that silicon monoxide sublimates and does not dissociate significantly during sublimation. Silicon monoxide is also widely used in optical coating technology, for electrically



**Figure 2**

Example for epitaxial  $\text{SiO}_x$  film growth. Substrate: slide glass for microscopy.

conducting films, and for corrosion-protective coatings [25–27].

The vaporization rate from a hot source into a vacuum (free surface vaporization) depends on the temperature of the source, the equilibrium vapor pressure of the material at that temperature, and the pressure in the vacuum chamber. Hence, stable temperatures are mandatory for reproducible film thickness. Silicon monoxide has an amorphous crystal structure, and is shipped as a granulate with an average grain sizes of about 0,5 mm (other grain sizes are also available).

The purpose of the vacuum is to reduce the gas pressure enough so that vaporized atoms have a long mean-free-path (at least some decimeters) and so they do not nucleate in the vapor to form soot.

Using a shutter, the layer thickness is controlled by the effective time (product of effective width of slits, number of slits, and number of rotations) the samples are exposed to the vapor stream jet. The actual deposition rate is about 15 nm/s at a substrate temperature of about  $100^\circ\text{C}$ .

The condensed silica layer is a thin inorganic film of about 500 nm thickness, which is tenaciously adherent to the substrate. Fig. 2 shows pictures of the epitaxial growth of the layer on glass. It consists of islands that gradually grow together with evaporation time.

The film thickness is measured by the interference fringe technique. A beam of incident light strikes the silicon



**Figure 3**  
Prosthesis (Model BiContact®, Aesculap, Tuttlingen, Germany) with interference colors due to SiO<sub>x</sub> layering (because of the surface roughness, layer thickness not measurable; equivalent layer thickness on a smooth surface would be about 500 nm).

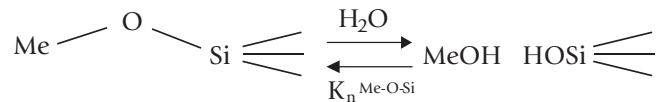
monoxide layer at a certain angle. A portion of the beam is reflected by the metal surface on which the film is layered, and the remainder of the beam is reflected by the film. The combined intensity of the net resultant ray at a given wavelength is a function of the phase difference between the two beams at a given wavelength. When the wavelength is continuously varied using a scanning double-beam spectrometer, the resulting spectrum is a continuous series of maxima and minima due to interference. From the refractive index, *n*, of silicon monoxide at the wavelengths of interest ( $0.2 \leq \lambda \leq 1 \mu\text{m}$ ,  $n \cong 1,9 \dots 1,85$ ), the distance between two or more minimum wave lengths and the number of fringes between those wavelengths allow the film thickness to be calculated. Fig. 3 shows an example of interference fringes on a femur prosthesis.

Since the film is only soluble in hydrofluoric acid, it has an excellent environmental stability. Its bonding to the surface is thought to be of chemico-mechanical nature by virtue of the irregularities produced by the sandblasting of the metal surface prior to the vapor deposition. The small silica particles develop a dense, adherent oxide coating network, which is of a glass like mineral nature, and a chemical constitution SiO<sub>x</sub>( $1 \leq x \leq 2$ ). The high vacuum environment, free of pollution, guarantees silica layers with reproducible characteristics and of high purity.

The joint between the methacrylate based bone cement and such a silica layer can be realized by the bifunctional silane bonder (3-Methacryloxypropyltrimethoxysilane),

which is a hybrid of silica and of organic groups related to resins. This surface modifier may theoretically form only one monolayer, but in practice the treated surface has an average coverage of 10 to 20 monolayers, corresponding to a layer thickness of up to 10 μm [28]. The silane functions to chemically modify a surface without contributing mechanical film properties of its own in the literal sense. Therefore, the silane has the part of solely a bonding agent. By a condensation polymerization, the silanol groups of the hydrolyzed silane form siloxane bonds with silica surfaces. The methacrylate groups of the silane can co-polymerize with the monomers of a methacrylate based polymer (Bis-GMA composite or methylmethacrylate, for example) which results in hydrolysis-resistant covalent bonds between the coupling agent and resin. Therefore, the silane acts as a bridge to bond the metal to the resin with a chain of bonds.

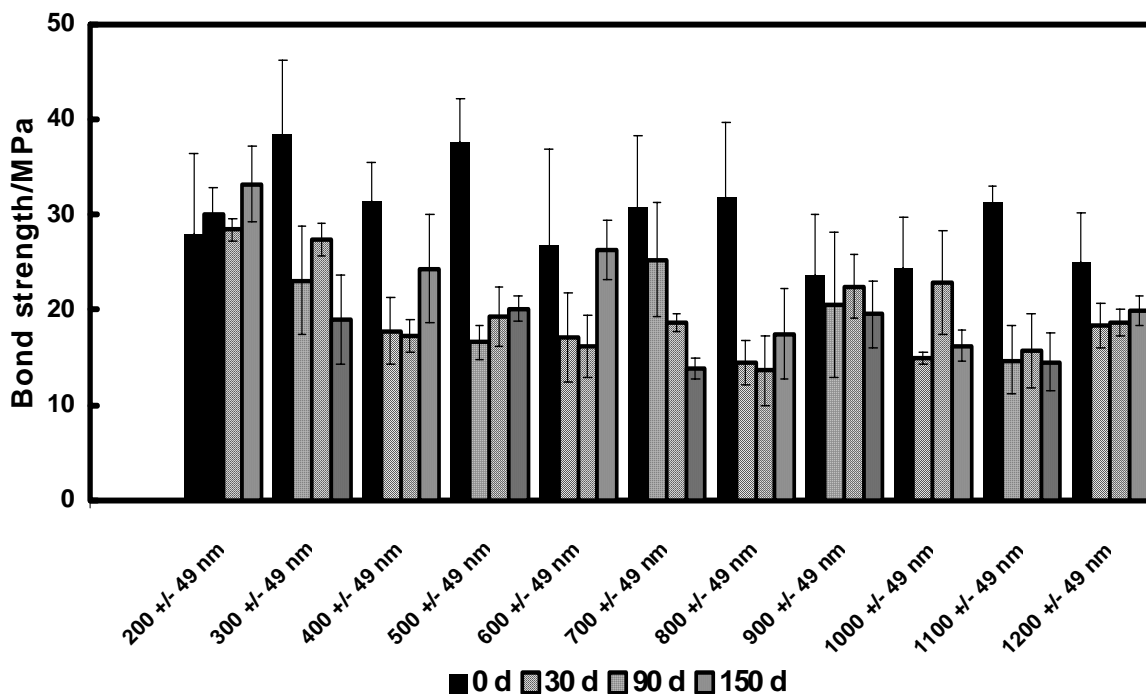
The silane coupling agent is expected primarily to improve the adhesion between resin and metal in the presence of moisture.



Good bonding stability across the interface requires that the reaction does not shift too far to the right in the presence of water. Contrary to the situation for a bare metal surface, the equilibrium state now lies on the left side of the equation because of the silica modified surface, which means more stable bonds in the presence of moisture.

Whereas the siloxane bond between silane and a mineral surface or a minerally enriched metallic surface is inorganic, with a high degree of ionic character, the bond between the silane coupling agent and the PMMA may be characterized as a bridge of covalent bonds. In the presence of a suitable silane, the double bond of the C atom of the PMMA-CH<sub>2</sub>-Group opens. After opening, a radical is available that co-polymerizes with the corresponding group of a suitable silane. Note that each kind of plastic needs its individual silane, depending on availability; PMMA and BisGMA have a silane in common: an alcoholic solution of N-beta-(N-vinylbenzylaminoethyl-gamma-amino-propyltrimethoxysilane).

The silica-/silane pretreatment can be utilized for metal surfaces as well as for ceramic surfaces [9]. At first glance, for a ceramic surface containing sufficient silica pre-conditioning by a silane should be sufficient. In particular, glass ceramic materials (crystal phase: feldspar), which are widely used in the field of dental prosthetics, consist of up to 70% silica. Note, however, that the surfaces of those ceramics after sintering are chemically dead and therefore



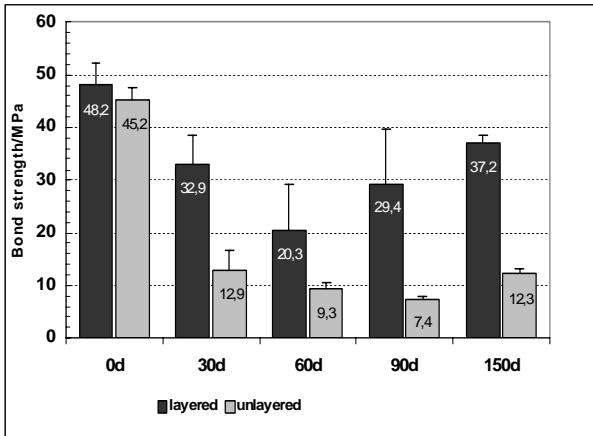
**Figure 4**  
 Bond strength vs layer thickness. Material: unalloyed Titanium samples adhered together with Refobacin®-Palacos®R. Before adhering together, samples were pre-coated by a protecting layer out of PMMA and BisGMA, similar to the layer protecting the silica layer on surface of the artificial stem. Without/with hydrolytic load 30 to 150 days; demineralized water, 37°C.

need activation prior to their treatment with silane. Moreover, although the coupling agent may have three reactive silanols per molecule, reactive sites on a mineral surface can be so spaced that no more than one silanol group per molecule can bond to the surface. The remaining silanol groups may condense with adjacent silanols to form a siloxane layer or remain partly uncondensed at the surface [28]. For both reasons, silicon monoxide enrichment can remove the described deficiencies, accomplish additional "dangling" bonds on the surface, and – enhanced by the obligatory sandblasting treatment prior to PVD layering – activate the surface. The surfaces of non-siliceous technical ceramics such as alumina- or zirconia-oxide can be modified in a similar manner.

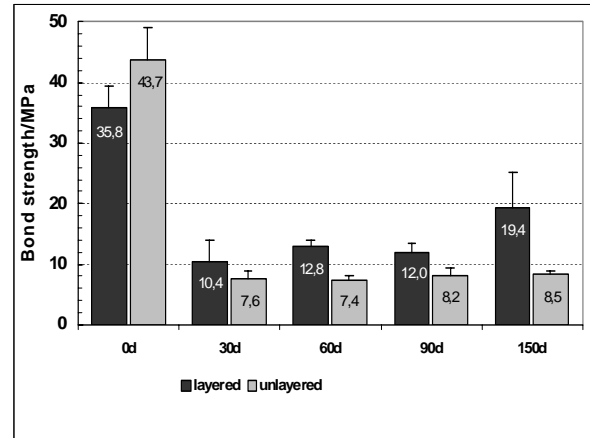
**Experimental results**

Experimental investigations of "dependence of bond strength on layer thickness with and without humid load" (Figs. 4 and 5), "dependence of bond strength on different periods of humid load and kind of alloys" (Figs. 6 and 7), and "crack concentration near the boundary between bone cement and metal stem" (Fig. 8) will be presented below. These studies confirm the long-term hydrolytic stability and the efficiency of the layer system. Particularly significant is how the dramatic reduction of development of cracks for coated stems underlines the potentiality of the new technology for cemented orthopedic femoral implants.

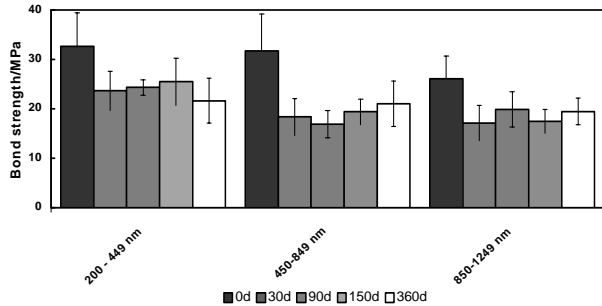
In a wide range of layer thickness the bond strength is independent of layer thickness, with a tendency to lower



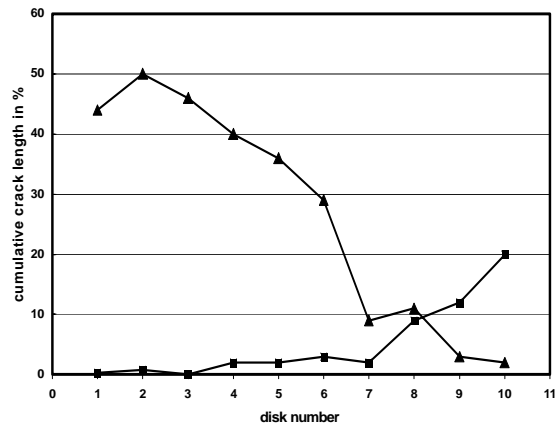
**Figure 6**  
Bond strength for TiAl6V4 alloy. Adhesive: Refobacin®-Palacos®R. Without/with hydrolytic load 30 to 150 days; demineralized water, 37°C.



**Figure 7**  
Bond strength for CoCrMo alloy. Adhesive: Refobacin®-Palacos®R. Without/with hydrolytic load 30 to 150 days; demineralized water, 37°C.



**Figure 5**  
Bond strength vs layer thickness. Layer thicknesses grouped into three classes. Material: unalloyed Titanium samples adhered together with Refobacin®-Palacos®R. Before adhering together, samples were pre-coated by a protecting layer out of PMMA and BisGMA, similar to the layer protecting the silica layer on surface of the artificial stem. Without/with hydrolytic load 30 to 360 days; demineralized water, 37°C.



**Figure 8**  
Crack frequency in the boundary region between bone cement and metal stem (TiAl6V4) with (squares) and without (triangles) layer system. Disk number 1 to 10: localizations along the femur stem from proximal to distal [29].

values and poorer stability under the influence of humidity beyond a thickness of about 1  $\mu\text{m}$  (Fig. 5).

The effect of immersion in water at 37°C on adhesive strength with and without a silica/silane interlayer is shown in detail in Figs. 6 and 7. Without the new coating layer system (conventionally cemented) high *initial* adhesive strengths of about 45 MPa were achieved, but after 150 days of storage in an humid environment, the adhesion strength decreased by approximately 75% for the TiAl6V4 alloy/Palacos R cement (Fig. 6) and 80% for the CoCrMo alloy/Palacos R combination (Fig. 7). For the silica/silane treated Ti alloy, the adhesive strength fell by 23% after 150 days storage. The corresponding number for the Co alloy was 46%. As a striking feature it should be mentioned that the stability for the Ti alloy was much better than that of the Co alloy [29,30].

A characteristic feature in Figs. 6 and 7 is the minimum of the bond strength in the center of the time scale. A plausible explanation of this anomaly is given by Hiss [31] and Müller [7]. These authors explain that the minimum is related to the strength minimum of bone cement stored in water, an effect caused by the competitive effects of water diffusing *into* the cement and of rest monomers diffusing *out* of the cement. The former diffusive process is believed to result in a weakening and the latter process in a strengthening of cement and hence of bond. A very slow completion of the silane bonds to its mineral chemical partners, which is known to need much time, may be another reason for the increasing bond strength beyond the center of the time scale.

Because of these effects, we speculate that after a period much longer than 150 days, the long term bond strengths again approximate the initial values, as Figs. 6 and 7 demonstrates a continuous increase of bond strength beyond a storage time of 30 days.

Figs. 8 shows a dramatic reduction of the fissure frequency for the layered stems [29], which is additional proof of the superior bond strength of the layered stems.

#### Acetabular component

##### Basics

For a cemented total hip arthroplasty, the acetabular component normally is machined out of ultra high molecular weight polyethylene (UHMWPE). PMMA cement is used to anchor the acetabular component to the bone of the acetabulum, just as PMMA cement is used to anchor the femoral stem into the reamed femur.

With respect to their adherence properties, two boundaries need to be considered: the boundary between bone cement and PE acetabular component, and the boundary

between bone cement and bone. Below, we describe in detail the conditioning steps needed to obtain a durable bond strength between the bonding partners.

#### Polyethylene as a bonding substrate

An essential improvement of bond strength to PE is possible employing plasma treatment. A plasma is an excited gas that consists of atoms, molecules, ions, free radicals, free electrons, and/or metastable species. The use of plasma is a common technique to pretreat polymers such as PE [32]. The plasma may be generated in air (corona discharge) or under reduced pressure (glow discharge). The major effects of plasma treatment in the enhancement of bond strength are cleaning, crosslinking and oxidation. Plasma *cleaning* may be more efficient than solvent cleaning. The excited species cleaning the surface are expected to have sufficient energy to displace low molecular weight contamination, e.g., water or additives remnant from processing. Although in most polymers this effect is considered as marginal, PE tends to become crosslinked. This can be of advantage since it prevents the development of a weak boundary layer at the interface of a joint by decreasing the diffusion of low molecular weight species from inside.

Oxidation is probably the most useful feature of plasma treatment. Oxidation may be due to the oxygen part of the plasma gas or to traces of oxygen being present in the treatment chamber. Polar groups such as unsaturated (C=C) and carbonyl (>C=O) groups are introduced into the surface region of the substrate, improving the wettability of the surface and hence also its adhesion properties. The improved joining properties are ascribed to the increased free energy of the polymer surface, especially for PE substrates [33].

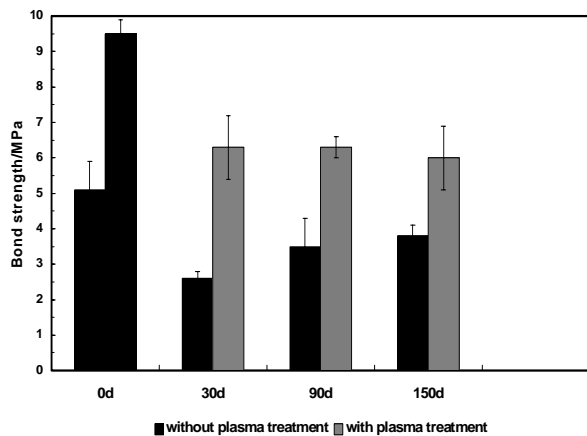
Fig. 9 shows the currently achieved bond strengths with and without plasma treatment for medical grade polyethylene (PE). The treatment results in a bond strength that is twice as high than without treatment. The stability under hydrolytic load is also much improved.

#### Bonding to bone

If mechanical interlocking were sufficient for a long-term retention between adhesive resins and bony substrates, questions of chemically bonding could be abandoned. However, questions of wetting might still be important as under the aspect of wetting the bonding partners, resin and bone, are incompatible, since resins have hydrophobic properties and bone has hydrophilic properties.

One has to differentiate between "compact (dense) bone" and "cancellous bone". Structures of compact bone are: osteon with the central *Haversian* blood vessel canal, *lacunae*, *canaliculi*, and *periosteum* which covers the outside.





**Figure 9**

Bond strengths between PE surfaces (sand blasted, adhesive: PMMA-BisGMA-Bonder and Refobacin®-Palacos®R) without (0d) and with (30d...150d) hydrolytic load (demineralized water, 37°C). The samples were plasma treated (20 min, plasma at 0.5...1 mbar partial pressure of O<sub>2</sub>).

Structures of cancellous bone are: *trabeculae* somewhat reminiscent to the osteon with lacunae and *endosteum*.

Bone is a type of connective tissue made up of cells (osteoblasts, osteocytes, osteoclasts) suspended in a matrix of calcium carbonate, hydroxyapatite, inorganic salts, and collagen fibers. In lamellar bone, the collagen fibers are laid down in lamellae layers in which all collagen fibers are oriented in the same direction. Collagen fibers in adjacent layers are oriented in different directions. The outer wall of bone shaft is composed of outer circumferential lamellae, which completely circle the bone.

Small dots in the bone wall are the nuclei of osteocytes located in lacunae (spaces in the bone matrix). The short tubular structures are called Volkmann's canals. Bone is constantly growing and at the same time reshaping. Osteoblasts are responsible for producing new bone matrix. Osteocytes are bone cells located in the lacunae and which have characteristic long processes running through the bone, being in contact both with other cells and with blood vessels and nerves. Osteoclasts are responsible for resorption of old bone matrix.

Micromechanical or chemical resin adhesion to compact bone differs considerably from the simple interlocking of resin to cancellous bone. This is because hydrophobic resins do not even wet the hydrophilic bone structures, and hence literally no adhesion between resin and substrate can be expected. Adhesion may nevertheless be achieved

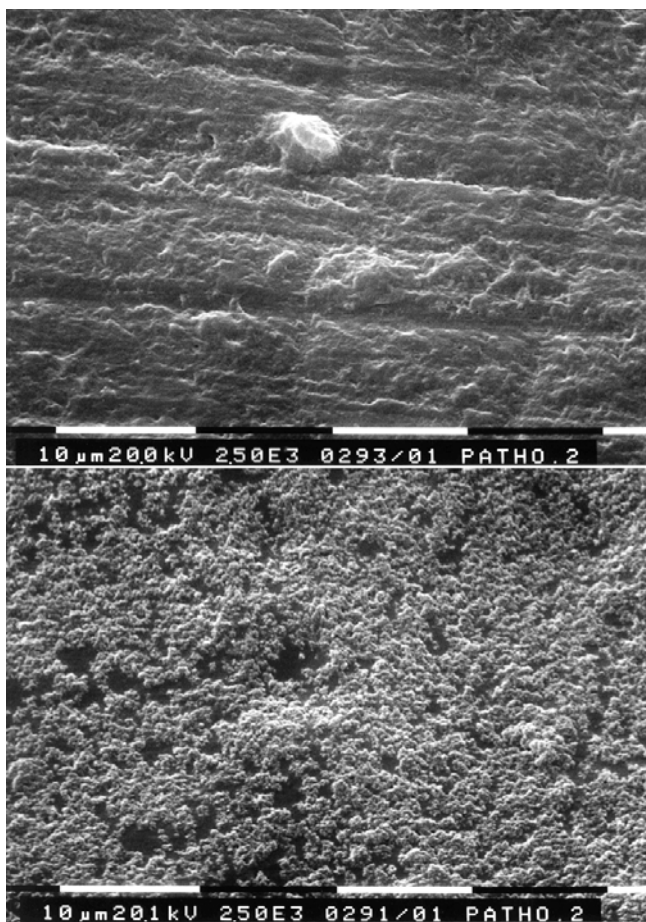
with the help of an interlayer system that forms a bridge between the chemically incompatible resin and bone bonding partners, and which brings the wettability properties (hydrophobic/hydrophilic) of both partners into accommodation [34].

Bone has the following special characteristics that must be taken into account when considering adhesion to it. These characteristics are in part reminiscent of human and bovine tooth dentin. [35,3,36–40]:

1. A high proportion of organic substances, especially collagen, gives rise to hydrophilic wetting behavior, which is in contrast to the hydrophobic properties of resin
2. Blood seepage, which is reminiscent of residual moisture and dentinal fluid flowing through the tubules connecting dentin with the pulp and transportation of dentinal fluid from the pulp to the dentin surface
3. Due to its preparation process, bone is covered with a layer of debris, e.g., blood, and abraded particles of other organic and inorganic matter, reminiscent of the smear layer covering dentin after preparation

Therefore, an adaptive approach is required to firmly bond a resin in particular bone cement to non-spongy bone. One may speculate about the feasibility of chemical bonds between resin and bone. We believe, however, that chemical bonds play a minor role in comparison with micromechanical interlocking to collagen.

Basically, the micromechanical retention between resin and compact bone surface is due to resin infiltration into the bone surface demineralized by acid etching to a depth of a few micrometers, thus exposing the collagen fiber network without damaging it (Fig. 10). The degree of retention depends upon the amount of uptake of liquid monomers into the interfibrillar spaces that were previously occupied by apatite mineral crystallites. It is thought that the durability of the resin-to bone bond depends upon how thoroughly the resin infiltrates these spaces, whether all of the exposed collagen fibrils are enveloped by resin, and how well the resin is polymerized. During the etching step, the debris layer described above is likewise removed. Both can be done by weak acids such as citric, maleic, oxalic, or phosphoric acid. EDTA-Fe-Na (ethylene diamine tetra acetic) can be used as an additive since it is suitable for the prevention of the denaturation of the collagen during and after demineralization. In preventing denaturation the ferric ion is especially important. As a further additive glutaric aldehyde can be helpful with protein fixation of collagen fibers.



**Figure 10**

SEM picture of a demineralized (below) vs. untreated (above) bone surface. The micromechanical retention between resin and compact bone surface may be basically due to resin infiltration into the bone surface demineralized by acid etching to a depth of a few micrometers ("hybrid layer"). The investigations were done on bone from freshly slaughtered sheep.

Under continued presence of humidity, after etching the collagen network stays suspended, like hair when it floats under water. However, if interstitial water is lost, the collagen fibers tend to stick together and subsequently collapse. Therefore, excessive drying by prolonged air blasting (e.g.) of the bone must be avoided, otherwise a condensed layer of collagen fibers, in which the collagen fibrils stick close together, may be formed, which would greatly impede resin penetration into the bone surface. If the collagen collapses during any step of the bonding procedure, the superficial porosity of the bone substrate will be reduced, and many of the sites available for resin infiltration will become lost. The collapsed collagen can form a barrier that prevents resin penetration throughout

the decalcified layer, resulting in poor quality of the hybrid layer and low bond strength [41].

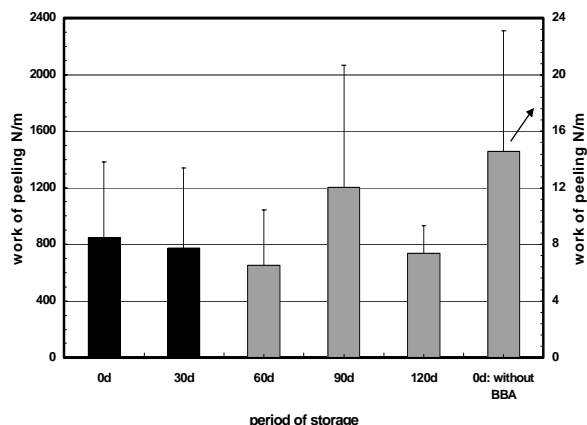
The etched bone surface still moist with the collagen exposed is wetted by amphiphilic monomers. Amphiphilic molecules generally have a low molecular weight, which means they are small and mobile. They are dissolved in water, ethanol, or acetone (e.g.: HEMA hydroxyethylmethacrylate, GM: glycerylmethacrylate, or 4-META: 4-methacryloxyethyltrimellit). HEMA can help to straighten collapsed fibers because of its hydrophilic properties. In addition to hydrophilic molecules, other monomers supporting film formation (e.g.: UEDMA: urethane ethylene glycol dimethacrylate), polymerization and cross-linking (mixtures of BisGMA (bisphenolglycidylmethacrylate) and TEGDMA (triethylen-glycol-dimethacrylat) (e.g.)) can be included. Amphiphilic molecules carry at one end a hydrophilic group, which enables them to penetrate the demineralized bone surface effectively. This hydrophilic group coupling to the superficial collagen is separated by a spacer from a methacrylate group on the other end of the molecule. The latter is incorporated into the polymeric network within the next bonding step.

The collagen fibers are infiltrated, impregnated, stabilized, and so prevented from collapsing. In the next step, the stabilized collagen network is infiltrated by a hydrophobic monomer that fills the interfibrillar spaces in the collagen network. For perfect infiltration it is mandatory that the collagen fibers did not collapse previously. The hydrophobic bonding agent may consist of BisGMA (bisphenol glycidyl methacrylate), TEGDMA (triethylene glycol dimethacrylat), UEDMA (urethane ethylene glycol dimethacrylate), Poly-EGDMA (polyethylene glycol dimethacrylate) or a mixture of these components. For a firm bonding layer, the infiltrated hydrophobic monomer in contact with the amphiphilic molecules must be light-cured, and the bone surface ready for bonding to a bone cement.

After polymerization, micromechanical retention to bone surface is achieved by the film, which incorporates the brush-like collagen network. This layer is called the "hybrid layer," which can be regarded as a "composite" of collagen fibers and resin. The penetration steps described may be limited by the fact that the gaps between exposed collagen fibers are very narrow (order of magnitude 100 nm), and hence the monomers that penetrate the exposed collagen fibers must have a very low viscosity.

#### *Experimental results*

In Fig. 11, the achievable bond strengths with and without the proposed layer system are depicted. The studies were done on bone pieces from freshly slaughtered pigs or



**Figure 11**  
Bond strengths in N/m [42] between bone surfaces (adhesive: Refobacin®-Palacos®R) with/without the proposed layer system (BBA) vs. period of hydrolytic load (demineralized water, 37°C). The investigations were done on bone from freshly slaughtered pigs or sheep.

sheep. Small blocks, 6 mm wide, 12 mm long, and 3 mm thick were cut from larger areas of the pelvis, with compact bone exposed on those sides on which the bonding layer system was to be applied. To assemble one specimen, two paired blocks were adhered together (Refobacin®-Palacos®R as adhesive), the surfaces of both blocks conditioned and pre-layered as described above. The 6 × 12 mm<sup>2</sup> contact areas were shielded to the middle of the surface (6 mm distance from the edges of the blocks) by a 30 μm thick, glossy, and greased aluminum foil. Since the bone cement did not adhere to the greased foil, a line of predetermined breaking points was established. These prepared "sandwiches" were symmetrically extended to the left and to the right with brass bars of the same cross section (overall length about 30 mm). Note that the rear sides of the two halves of the sandwich had cancellous bone exposed so that they could efficiently be fastened to the brass extensions. With the help of a three point bending arrangement, we were able to measure the work of fracture (peeling work) in N/m as a criterion of the quality of adherence [42]. The experiment was done with and without longtime storage in water at 37°C.

Note the different scales in Fig. 11. The right handed scale is magnified by a factor of 100, showing that the bond strength of pretreated bone is roughly two orders of magnitude larger than the bond strength of the unconditioned samples.

### Tendon- and Ligamentoplasties

Prosthetic replacement of injured (hyper-flexed, ruptured) tendons and ligaments presents problems that have not yet been satisfactorily solved. The hyper-flexed tendon or ligament can be repaired with conventional surgery. A ruptured tendon or ligament, however, may be surgically repaired by suturing, while the reconstruction or replacement of an unreparable tendon or ligament often uses autogenous or synthetic materials.

Autogenous reconstructions imply harvesting prosthetic substitutes from other parts of the body of the same individual. This process leads to defects and donor site morbidity. However, because of the long healing periods of such transplants, the use of synthetic grafts merits consideration for such a procedure. Synthetic materials have been clinically used for many years. The theoretical advantages of alloplastic grafts are obvious: unlimited availability, intact autogenous structures, minimization of operative time and trauma, technically simpler surgical procedure, immediately functional stability, and a shorter healing process.

Textile constructs for tendon- and ligament replacement have been employed in orthopedic surgery for many decades. First reports by Lange on the implantation of a silk ligament in the knee joint date back to 1903 [43], but proved to be of no use only 3 years after surgery. In the following decades the implantation of artificial materials was sporadically reported, mostly using silk [44]. The development of plastic materials opened a new area in the 1960s. The replacement of the anterior cruciate ligament in dogs was the first application reported [46]. The first human application was described by Mironova in 1978, who implanted polyester ligaments in 262 patients over a period of 15 years, reporting a 91% success rate [47].

The 1970s showed an increased interest in alloplastic ligaments, resulting in commercial products such as the Proplast® ligament (Vitek-Inc., Houston, Texas; USA)[48] and the Polyflex® ligament (Richard,, Memphis, Tenn., USA). Both products showed poor results and had to be removed in numerous cases due to rupturing and causing inflammatory reactions in the joints where they had been implanted. Experimental data revealed insufficient mechanical properties [49].

In 1977, Jenkins reported on the use of carbon fiber for tendon replacement, which had been in clinical trials since 1973 [50]. Reports on the application to replacement of the cruciate and other ligaments in the knee, and use in other joints followed [50,51]. After initially promising results, the carbon fiber ligaments produced severe problems in clinical application. It was shown that their poor resistance to cyclic bending forces led to early

ruptures of the fibers, releasing wear particles that could spread throughout the joint, leading to "black joints" and initiating an inflammatory response. Particles were even transported to regional lymph nodes [52,53]. The function of the carbon fibers as a scaffold for the ingrowth of connective tissue and for bony ingrowth in the osseous canal, which had been anticipated, could not be proven [53]. Also, composite grafting with autologous material or the coupling of resorbable polymers to the surface of the ligament could not outweigh the side effects and complications [45].

In 1975, Kennedy described the implantation of a polypropylen ligament (Kennedy-LAD<sup>®</sup>, 3M, St. Paul, Minn., USA) for the first time [54,55], other reports followed [56–59]. This prosthetic was implanted mostly as augmentation for autologous materials, allowing temporary load sharing, while accepting its weakening and rupture with time. All reports stress the good biocompatibility of polypropylen, but permanent application as ligament prosthesis was not recommended.

Polytetrafluoraethylen, (Gore-Tex<sup>®</sup>, W.F. Gore&Assoc., Flagstaff, Ariz., USA) a well established biomaterial used in vascular surgery, in a braided form was also used in ligament replacement surgery. This ligament showed the best initial load bearing properties of all commercially available alloplastic ligaments. First reports were published in 1983. Bony ingrowth of the ligament in the osseous canals was demonstrated. Despite these aspects and promising first clinical reports, the long term clinical results were disappointing. Frequent ruptures and synovial reactions within the implanted joints were described [46,60].

A different constructive approach was taken for the Dacron<sup>®</sup>-ligament, which was first implanted in the treatment of disruptions of the acromioclavicular joint and in tendon replacement. This ligament used a braided 4-fold inner part enveloped in a knit cover, which was supposed to improve tissue ingrowth and lead to an improved adaptation of its elastic properties to the human cruciate ligament. Also, this ligament showed good initial, however poor long term, results, with a progressive deterioration and high rupture rate [61].

Besides the polypropylen ligaments, today only the different polyester ligaments play a role in clinical application [62]. Examples are the Leeds-Keio<sup>®</sup> ligament, the Trevira-hochfest<sup>®</sup> and the Proflex<sup>®</sup> ligament.

The Leeds-Kejo<sup>®</sup> ligament was firstly implanted in Japan 1982, also later in the UK. Until 1988 some 20.000 ligaments had been implanted. The reported results are few and contradictory [63–65].

The Trevira<sup>®</sup> ligament consisting of polyethylenterephthalat has been clinically in use since 1980 [66]. It was first used in the cervical spine for stabilizing procedures. Adapted for joint applications, it was implanted in the knee as a cruciate ligament replacement and as an augmentation of autologous transplants. It shows only minor wear and inflammatory response in animal trials as well as in clinical experience. Clinical results are good during the first years, while long term studies have not yet been reported. A modified over the top implantation technique can improve the ligament longevity.

The common problem of all alloplastic nonresorbable ligaments is weakening of the structure due to wear, leading to rupture rates between 5% and 25% per year [67–69]. Analyzing 117 surgically excised alloplastic ligaments after failure as anterior cruciate ligament prostheses, Guindoin [70] summarized the major mechanisms that led to failure as inadequate fiber abrasion resistance against osseous surfaces, flexural and rotational fatigue of the fibers, and loss of integrity of the textile structure due to unpredictable tissue infiltration during healing.

According to Letsch [71], the anchoring mechanism of an alloplastic ligament is one of the crucial points of the system. The maximum load capability of most fixation systems is 10% to 25% of the load capability of the alloplastic ligament itself, and therefore is the limiting factor of the system. Moreover, the textile structure is weakened or damaged by fixation elements like screws or toothed staples, leading to loosening of the ligament and additional wear [72].

The unsolved problems of alloplastic nonresorbable ligament structures has brought the resorbable ligaments into focus. Even if the latter provoke an inflammatory response, they have the advantage that inflammation ends once the resorption is complete. Polydioxanon (PDS<sup>®</sup>) has been widely used since 1979 [73], as augmentation in cruciate ligament surgery, and is available in different constructions. Clinical and experimental comparative testing did not show a significant advantage compared with non augmented transplantation. The decrease in load bearing capability of the resorbable ligament during resorption leads to mechanical properties that cannot compete with those of nonresorbable structures.

It becomes clear that, despite the development of a variety of synthetic implants and better knowledge of ligament biomechanics, there is currently no prosthesis that shows satisfying long term results. In fact, the life span of ligament prostheses are rather short. However, this should not lead to the conclusion that synthetic grafts are generally unsuitable. Instead, it is evident that there is a need to reconsider the approach and to develop a new generation

of implants and fixations techniques. In particular, the method of *fixation* of ligament prostheses requires attention. Currently used fixation techniques allow micro movements of the ligament, which lead to friction against bone, causing wear and implant failure of the entire prosthesis.

The aim of our investigation was to reduce the deficiencies of the fixation techniques that have been so far applied. New ideas are proposed for the anchoring of textile structures by using modern adhesive methods that aim for a more physiological bone-ligament junction [74]. Utilizing adhesive methods also means a suitable selection of the material out of which the artificial tendons and ligaments are plaited, since not all plastics are appropriate for adhesive techniques. Highly desirable are plastics that fulfill both the clinical necessities and the requirement that their surface can be effectively conditioned by plasma treatment.

The fixation technique must result in an anchorage of the alloplastic prosthesis that is strong enough to prevent slippage. Moreover, the fixation technique must resemble closely as possible the natural load flux into the bone. The techniques currently utilized lack the tensile characteristics of physiological load flow, and thus they are unable to provide optimum distribution of forces to the bone, since fixation of artificial structures is achieved with staples, screws, and clips, which of course are accompanied by a very unfavorable distribution of forces among tendon, fixation tool, and bone.

As an example, we describe the presently used fixation technique for the reconstruction of the anterior cruciate ligament (ACL) of the knee using a Trevira ligament [75]. Note that such a ligament is unsuitable for the application of adhesive techniques since it consists of many very thin threads, difficult to prepare for adherence because highly viscous adhesives like PMMAs and their modifications are not able to penetrate threads. For analogous reasons plasma treatment is also difficult. The ligament is first fixed at the femur. After turning back the windings outside the over-the-top passage, the ligament is laid flat on the femur. The femur is marked and a staple is driven in to fix the ligament. The end of the ligament is cut until nearly 2 cm and placed under the muscles. The final fixation of the ligament takes place with a second staple after marking the tibial cortex. The end of the ligament is also cut to almost 2 cm and placed carefully and flatly under the pes anserius.

In the long term, the majority of ligament prostheses result in insufficient fixation strength, demonstrating their deficient anchorage to the bone. The low fixation strength, corresponding to fixation failure at forces of

140–180 N, has been found to be the limiting factor of most of the ACL replacements. Such forces compares unfavorably with the fixation strength of goat native ACLs (e.g.), which tolerate loads in excess of 1 kN.

In this paper, we discuss two examples describing the usefulness of adhesive instead of conventional fixation techniques. The adhesive technique is described for a tendon replacement, and may be applied with minor changes for artificial ligaments as well.

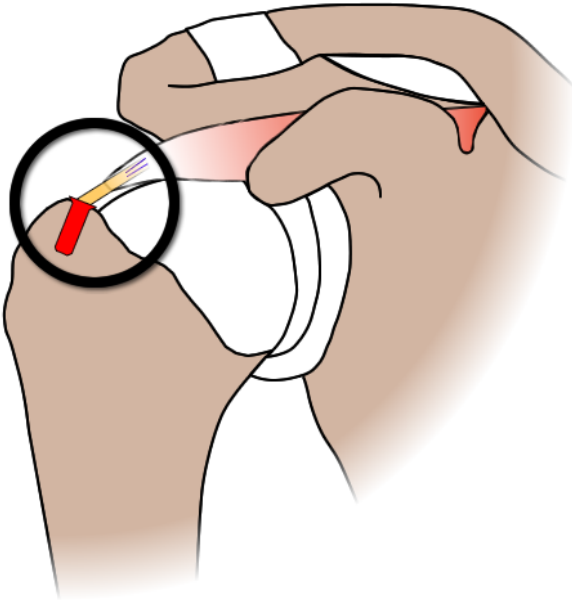
#### *Supraspinatus tendon*

##### *Basics*

First, we focus on the replacement of the supraspinatus tendon from the rotator cuff group, using alloplastic textile structures. The term "rotator cuff" is used to describe the group of muscles and their tendons in the shoulder that helps control shoulder joint motion. The supraspinatus muscle is at the top, the subscapularis in the front, and the infraspinatus and teres minor are behind the shoulder. These muscles attach to the head of the upper arm by way of their tendons. The tendons fuse together, giving rise to the term "cuff." Although each muscle acting alone may produce an isolated rotational movement of the shoulder, the role they play together is to help keep the head of the upper-arm ball centered within the socket.

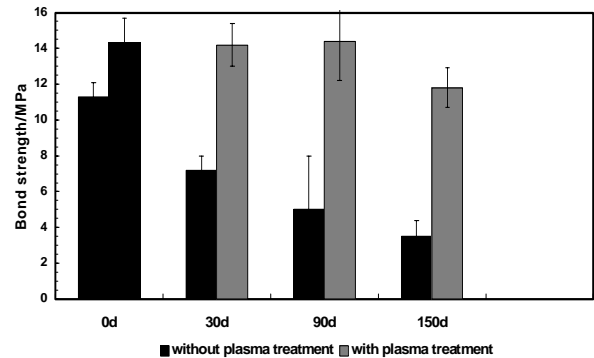
In case of a fresh traumatic rupture, the implant is used as an augmentation corresponding to the suture techniques that are in use today, connecting the ruptured tendon directly to the bone, where it can heal under stress protection by the implant. After healing, the implant functions as a permanent augmentation, which is favorable considering that the tendon heals with scar formation from tissue less mechanically stable than the original tendon.

Another application concerns patients with defects in the rotator cuff due to degeneration and old rupture. Today, this defect can only be corrected by extensive plastic methods, transposing autogenous tendon material from other sites [76–78]. Even if – due to biological reasons – a replacement cannot restore function in all cases, it is to be expected that using the novel implant in these situations will reduce pain by restoring the joint anatomy [79,80]. Technically, in these cases it will be necessary to bridge the defect by up to three implants, depending on the size of the defect, in order to get a good distribution of forces. Additionally, it will be necessary to enhance the formation of connective tissue between the implant cords to restore the cuff as a barrier between joint and bursa in order to avoid irritation. This can be accomplished either by local tissue or by additional resorbable implants.

**Figure 12**

Overall view of the proposed shoulder fixation element in situ. Banjo bolt with alloplastic PVDF tendon adhesively inserted.

The alloplastic tendons presently being investigated were braided out of polyvinylidene fluoride (PVDF: common brand names: Fluoradon, Kynar, Solef). PVDF is a semi-crystalline, semi-opaque and white, engineered thermoplastic that is melt processable. PVDF has good temperature characteristics, and good resistance to general chemicals, (though not as good as PTFE's), abrasion, and radiation. It is somewhat stiffer and stronger than most (being melt-processable) fluoropolymers, which facilitates adhesive techniques for threads. The elongation at break is 50%, the tensile modulus 1 to 3 GPa, the density 1.76 g/cm<sup>3</sup> and it has a highly dipolar molecule. PVDF radiation resistance (beta, gamma) is good, and therefore it may be sterilized by beta-radiation, as is standard for many orthopedic devices. The desired form is known as the  $\beta$  phase or Form I, in which the predominantly "head to tail" polymer chains have an all-trans extended planar zig-zag form, with the dipoles of adjacent chains parallel to one another. This pattern is formed from the more common  $\alpha$  phase (Form II) by mechanical deformation followed by electrical polarization in a very high electrical field. In practice, both uniaxial and biaxial mechanical orientations are used. Applications of PVDF include pipes and fittings, bearings, linings, and vessels (all especially for the chemical processing industry), wire insulation and piezo-electric devices. In medical applications, PVDF has been in use as a *suture* material for years.

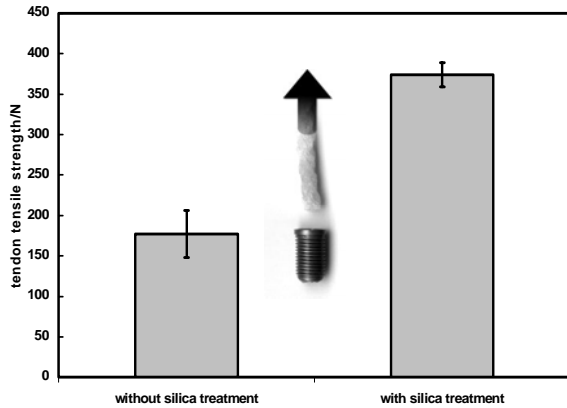
**Figure 13**

Bond strengths between PVDF surfaces. Adhesive: self curing BisGMA. Several kinds of surface treatment (sandblasting and O<sub>2</sub>-plasma vs. solely sandblasting) without/with hydrolytic load (30 ... 150 days (d) in demineralized water, 37°C).

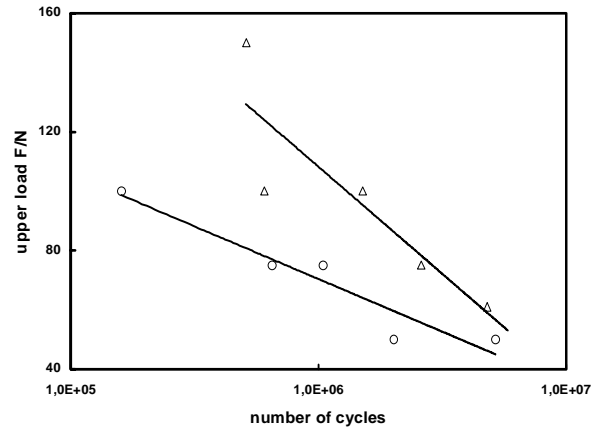
Fig. 12 depicts an overall view of the presently proposed prosthesis as an example. The fixation element [34] consists of a banjo bolt (thread M4...M6 or hollow tapping screw), the alloplastic PVDF tendon axially inserted. The screw has been machined out of titanium or a suitable titanium alloy (TiAl6V4, e.g.). The inner walls of the screw have been PVD layered with a silicon monoxide coating, silanized, and finally layered with a very thin film of PMMA/BisGMA coating, which due to its low viscosity in the unpolymerized state and its hydrophobicity has perfect wetting properties on a surface enriched by silicate. The PVDF tendon consisting of 8 slackly plaited strands (36 threads bundled into a strand) has been plasma treated and fixed inside the coated banjo bolt by a BisGMA adhesive, the viscosity of which is adjusted such that it can wet each strand or even each thread when the adhesive is applied under pressure. The adhesively assembled fixation element (screw and tendon) is allowed to cure overnight.

Fig. 13 depicts the bond strengths achievable on PVDF samples (cylinders of 6 mm diameter, flat fore-parts in pairs adhered together after conditioning by different plasma treatments).

For clinical application as replacement or augmentation of the natural tendon, first a hole in the bone is drilled at the site marked on the humeral head for tendon reattachment. The bolt implant is then screwed into the hole so that the top of the implant is at or slightly above the bone surface. The implant must not protrude too much from



**Figure 14**  
Retention of PVDF tendon and fixation element. Pulling at fixation element (banjo bolt) and PVDF tendon until break. Diameter of tendon 2,5 mm. Tendon with tight network. Prosthesis 24 hours soaked in boiling physiological salt solution at 100°C before being tested.



**Figure 15**  
Fatigue amplitude test. Cyclically pulling at fixation element (banjo bolt) and PVDF tendon. Angle between axis of fixation element and tendon about 120 degrees. Lower load 10% of upper load, sinusoidal time dependence of load, 3 cycles per second. Diameter of tendon 2,5 mm. Open triangles: tendon with tight network, open circles: tendon with loose network.

the surface, otherwise it could give cause to irritation of the neighboring tissue with inflammation of the bursa (small sac filled with lubricious fluid). The bursa is located between the tendon and the bone of the humeral head and cushions the tendon from the bone, thereby reducing the friction between the moving structures.

The free end of the PVDF tendon is sutured to the supraspinatus tendon in a way that allows good interconnection between tissue and graft so as to accelerate healing and allow early load bearing. After implant surgery, patients should be able to start active exercise with restrained force within the first week.

Three to nine months are required after implantation to accomplish bony healing. This process, where bone grows into the implant, is called osseointegration. In the meantime, the quality of the mechanical screw fixation is responsible for the distribution of forces.

**Experimental results**

From in vitro experiments we have learned (Fig. 14) that the presently proposed implant allows a retention force (measured by axially pulling on ends of fixation element and tendon simultaneously) of at least 350 N. This force is sufficient to keep the implant stable under body conditions for at least several months, allowing the body to heal the tendon by scar-formation and adapting it to the load capability required for individual patient activities. These adhesively fixed tendons have the advantage of a very

smooth power flow between the PVDF tendon and the screw, much smoother than attainable by clamps. Moreover, a particularly space saving kind of attachment is at hand. Note that it is possible to machine specifically adapted screws that allow fixation of the PVDF tendon under different angles between the axis of the screw and the tendon. Because of the smooth power flow from the tendon into the screw, the risk of injuring and weakening the tendon by notch effects, as they are typical for clamps, is much lower.

These advantages could also be helpful replacing the ACL in knee surgery. As mentioned above, one of the main problems of artificial ACL reconstruction is the insufficient fixation stability to the bone. With the proposed adhesive technique, it could be possible to realize a more stable fixation of the artificial tendon to the bone. In addition, a more physiological load transfer from the artificial ligament into the bone seems to be achievable. Although clinical data are missing, experimental work shows promising results for the use of artificial ACL reconstruction in the near future. Fig. 15 shows fatigue amplitude tests that lead to fatigue failure due to cyclic forces. Such a diagram relates both to material properties and structural geometry. It requires one specimen to be run to rupture in order to provide just one point on the curve. The frequency of cyclic loading is usually low (presently 3 cycles per second between maximum and minimum loads) such that one single test may go on for

several days or weeks. A graph of the maximum stress force,  $F$ , in newtons (N) vs. cycles to failure (S-N curves) is plotted. By successively lowering the maximum stress, specimens fatigue-tested without rupture are determined. The maximum stress, that does not result in failure can thus be determined. This procedure provides important guidelines for the maximum serving stress that the artificial tendon in combination with the fixation element can withstand (Fig. 15).

## Conclusions

When inserting a prosthesis into the human body, not only one but several material classes are involved. Up to now, clamping and screwing of the structural parts of a prosthesis has been the normal procedure. In the present contribution, it is proposed and demonstrated that joining by adhesive techniques can also play an important and useful part, provided the stability under the conditions of use within the human body is adequately considered. Within the scope of adhesive techniques, -resistance to the attack of humidity (besides mechanical load) is mandatory for clinical success. The present work maintains the thesis that achieving stable bond strengths means selecting individually and suitably adapted pre-treatments of the material surfaces.

## Authors' contributions

RM conceived in the study, participated in the design of the study and drafted the manuscript. HJE and DCW carried out the clinical and experimental studies, MW carried out experimental work. OP and FUN coordinated the clinical part of the work. All authors read and approved the final manuscript.

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