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Review Article

Elastomers for the Development of Orthopaedic Implants - A Review

D.Abela[*1], **A. Rochman**[1], **J. Buhagiar**[2], **P. Mollicone**[3], **P. Schembri Wismayer**[4]
[1] *Faculty of Engineering, Department of Industrial and Manufacturing Engineering, University of Malta, Msida, Malta*
[2] *Faculty of Engineering, Department of Metallurgy and Materials Engineering, University of Malta, Msida, Malta*
[3] *Faculty of Engineering, Department of Mechanical Engineering, University of Malta, Msida, Malta*
[4] *Faculty of Medicine & Surgery, Department of Anatomy, University of Malta, Msida, Malta*

Abstract. There has been an increase in the use of elastomers in the biomedical industry. Recent developments in utilising elastomers for use in orthopaedic implants has shown the great potential of these materials for long-term implantation. Elastomers are being developed for applications in tissue engineering, polymeric scaffolds and synthetic implants, all with the aim of repairing or maintaining orthopaedic joints in working order. The aim of this review is to discuss current developments in elastomeric orthopaedic implants and their most utilised materials namely silicones, polyurethanes and hydrogels. Polyurethane and silicone elastomers are commonly used in bulk implantable devices due to their good mechanical properties, chemical resistance and biocompatibility. Other materials such as polycarbonate urethanes (PCUs) are being utilised as means to protect the joints due to their superb mechanical properties and wear characteristics. The range of applications of elastomers vary from hip joint replacements, such as in the case of the TriboFit® implant, meniscal implants, and first metatarsophalangeal joint replacements. More recently hydrogels have been utilised as coatings for increased lubrication in joint replacements, as a substitute for articular cartilage. Applications of hydrogels vary from improving the collagen and proteoglycan content of the joint to improving the load distribution across the joint in arthritic knee joints. The use of elastomers in orthopaedic implants is still in its infancy; and whilst a large amount of the research being done is still in the prototype stages, the potential of these materials and devices is virtually unlimited.

Keywords: elastomer, bioelastomer, biomaterial, biomedical, implants, orthopaedic

1 Introduction

The application of elastomeric polymers for biomedical implants has recently been on the rise. Elastomers are a sub-class of the polymer family, which have a low amount of inter-molecular forces, which together with their flexible and soft nature allow them to have a particularly high elongation (Özdemir, 2020). As such, elastomers are materials which are capable of showing large and rapid strain in response to an applied stress (Shanks et al., 2013). In general elastomers have large toughness values, having the ability to absorb energy under stress. Additionally, the term 'bioelastomer' refers to those elastomers which exhibit good biocompatibility in the implantation site, a glass transition temperature below the body temperature (35–40°C), while also having the ability to return to at least 1.25-fold of their original length after 1 minute of release if stretched to 1.5-fold of their original length for 1 minute, maintaining stretch stresses in the range of 0.1–20 MPa (Shi et al., 2009).

While a large portion of the use of elastomers in the biomedical field still remains in the sector of non-physiological contact biomedical devices, such as syringes and disposable gowns for surgeons and operating tables, there has been an increasing interest in the use of these materials for implants with physiological contact including orthopaedic applications, dental reconstruction, contact lenses, cardiovascular devices, catheters, sutures, adhesives, and membranes amongst others (McMillin, 2006).

There has also been an interest in replacing traditionally metallic implants with polymeric ones, creating lighter devices due to the inherently lower density of polymers. Simultaneously, complex shapes can be created with the possibility of large-scale production, thus greatly reducing

Correspondence to: D. Abela (dylan.abela.14@um.edu.mt)

manufacturing and processing costs while creating flexibility in the design of the material for specific applications (Festas et al., 2020).

There are three main types of elastomers which are used in biomedical devices, namely: (i) commodity elastomers, (ii) medical-grade biodegradable elastomers for short-term physiological contact and (iii) medical-grade non-biodegradable elastomers for long-term physiological contact (Basak, 2021).

All implantable bioelastomers need to satisfy the twin requirement of surface compatibility and adequate long-term mechanical properties which are dependent on the application *in vivo*. Bioelastomers have to be tested on the medical device for which they are intended, since their manufacturing process may affect the long-term capability of the material, by using standard practices issued by recognised institutions, such as Directive 90/385/EEC, consisting of EU regulations regarding implantable medical devices.

Table 1 shows a list of the elastomer properties which are required for orthopaedic implantation. Validation methods for the mechanical properties required are dependent on the application. For instance the validation of cardiovascular and pressure devices are different as shown by Kanyanta et al. (2010) for a polyurethane elastomer used in a cardiovascular application and by Courtney et al. (2001) for a shock absorbing elastomer composite, where the former material was tested under uni-axial, planar and equibiaxial tension, stress relaxation, creep and cyclic loading, while the latter was tested for impact absorption characteristics.

To predict the durability and fatigue lifetime of an elastomer, the biaxial stress-deformation at high strain rates of the elastomer has to be known. The elastomer will fail due to fatigue when it experiences a stress which is far below the static mechanical strength (Yoda, 1998).

Elastomers which have to be inserted in a physiological environment have to utilise the least amount of toxic catalysts and leaching polymer additives to reduce the occurrence of unwanted or damaging reactions, which is also affected by the manufacturing process. Silicones and polyurethanes are those elastomers from which the smallest amount of toxic chemicals are extracted (Yoda, 1998). Finally, the bioelastomer has to be sterilised before making physiological contact to remove any components which might be detrimental to the function. Each elastomer has its own specific and applicable sterilisation technique. Some of these techniques are mentioned in Table 1.

This paper sets out to compile a review of elastomeric materials currently being utilised for the development of orthopaedic implants, including silicones, polyurethanes and hydrogels. Following this, a review of the current developments being made in the field of orthopaedic implants will be presented, starting with a case study on a total hip replacement followed by the evolution of first metatarsophalangeal joint replacements and ending with elastomers used as meniscal implants in the knee joint.

2 Elastomeric Polymers for Biomedical Use

2.1 Silicones

Silicone (also known as polysiloxane) is the most common elastomer currently used in the biomedical industry. It is composed of silicon, carbon, oxygen and hydrogen (Shit et al., 2013). The physical properties of this material are determined by the chain length and the degree of cross-linking. Silicone has good biocompatibilty and excellent bio-durability with host tissue in orthopaedic implantation sites. These characteristics give silicon the ability to be in a physiological environment while maintaining minimal tissue interaction and keeping deterioration of the properties to a minimum over a long period of time. Moreover, the response of the tissue on the silicon is very low since the material is resistant to attack by the surrounding tissue and cannot be metabolised by other organisms. This high resistance to external attack originates from the ionic Si-O bonds in the structure, giving high bond strength (Zare et al., 2021).

Silicones have been used in a range of applications, varying from catheters (Folysil® and Prosys® Foley catheter) and other short-term implants to inserts and other implants used to replace or repair parts of the body for long-term use, such as mammary implants (Allergan Natrelle®, Mentor® Memory Gel®). As early as the 1960's, implants were being developed in the field of or-

Property	Description
Physical Properties	High elasticity, moderate strength, durability, stability
Manufacturability	Injection moulding, extrusion, solvent casting, calendering
Biocompatibility	Non-allergenic, non-carcinogenic, non-mutagenic, non-toxic, hemocompatible
Sterilisability	Steam autoclaving, dry heating, ethylene oxide gas, electron and gamma irradiation

Table 1: List of properties required by elastomers for orthopaedic implantation (Özdemir, 2020; Shi et al., 2009; Yoda, 1998).

thopaedics, where silicone was used as a spacer to replace tissue and cartilage function in the finger joints. It was also adopted in the total knee replacement procedure, where it acted as a shock absorber between the femoral and tibial components (Moximed® Calypso® Knee System) (Zare et al., 2021). Medical-grade silicone is available in different varieties depending on the application. Typical silicone is compounded using very fine and pure amorphous silica which is used as a filler to improve the tear and tensile strength. Any fillers which remain present will affect the blood compatibility of the silicones. Studies are currently under way to investigate the possibility of processing silicones without fillers utilising polydimethyl-siloxane as the main backbone of the polymer chain, terminating in acetoxy groups, such as in the elastomer Cardiothane 51 (Yoda, 1998).

Silicones with biocompatible fillers are prepared using modified silica in two ways: a) silica bonded with antithrombogenic heparinoid agent (to prevent blood coagulation); and b) silica bonded to reactive H-Si groups obtained by the reaction of the silica with methyldichlorosilane. Such silicones exhibit good mechanical properties as well as excellent tissue compatibility.

Silicones tend to exhibit good blend compatibility with various block copolymers such as SBS (styrene-butadiene-styrene) and SEBS (styrene-ethylene/butadiene-styrene). These blends yield good surface and processing properties. Polypropylene also exhibits good blend compatibility when added to silicone modified block co-polymers, giving a uniquely favourable balance of properties intended for biomedical use. These silicone elastomer/PP blends contain no phtalate plasticisers and still exhibit silicone-like surface properties coupled with thermoplastic processability and improved elastomer strength properties.

Thermoplastic silicones include a range of silicone co-polymers and block co-polymers, such as silicone-urethane and silicone-polycarbonate. Some of these silicones have been developed with exceptional blood contacting properties and reasonably good physical properties. The properties of these materials vary greatly from typical silicones in that they exhibit higher mechanical strength amongst other varying properties (Arkles et al., 1983). A common silicone-urethane used in biomedical devices is Cardiothane 51, which is a co-polymer of polydimethyl-siloxane and aromatic polyether urethane, cross-linked by the interaction of acetoxy-terminated siloxane blocks with substituted urethane nitrogens. The properties related to this material include good biocompatibility (especially in cardiovascular applications), excellent fatigue strength, toughness and flexibility (Nyilas et al., 1977).

2.2 Polyurethane Elastomers

Polyurethane elastomers (PUs) are considered amongst the best performing medical-grade polymers available in the biomedical industry. Their biological and mechanical properties make them suitable to be utilised in a range of implantable medical devices, since they exhibit an exclusive combination of biocompatibility, biostability, flexibility, toughness and durability (Christenson et al., 2007; Khan et al., 2005b). Table 2 shows a list of properties and characteristics for silicone compared to polyurethane.

PUs typically have a more complex structure than most common polymers like polystyrene or polyethylene which are composed of one or two monomer units. Instead, they comprise of: (a) a flexible polyol (or macrodiol), also referred to as the soft segment, having a stiff part based on a diisocyanate and (b) a chain extender, referred to as the hard segment (Kébir et al., 2017). The ability to utilise different variations of the three components during processing leads to PUs with varying mechanical and physiochemical properties (Christenson et al., 2007; Khan et al., 2005a). The structure of PUs is normally a two-phase structure comprising of aggregated semi-crystalline micro-domains dispersed in an amorphous structure. As such they are referred to as segmented block co-polymers. The predominant linkage which is present in the soft segment will identify the type of PU, for instance poly-(etherurethanes) contain ether moieties, poly-(esterurethanes) contain ester linkages, while polycarbonate urethanes (PCUs) contain carbonate linkages (Elsner et al., 2017).

The first biomedical PUs, poly-(ester urethanes), were found to be unsuitable for implantation due to rapid hydrolitic deterioration of the aliphatic polyester soft segment in the PU. Subsequently, poly-(ether urethanes) were utilised as a substitute due to their improved hydrolitic stability. However, implants made from softer grades of the material still failed due to oxidative deterioration originating from metal-ion oxidation and environment stress cracking (Wiggins et al., 2001; Zhao et al., 1990). Failure of PU-based implants such as breast implants and pacemaker leads in the 1980s led to the scrutiny on the suitability of the material for long-term implantation (Elsner et al., 2017). PCUs were subsequently developed to compensate for the problems related to stress-cracking and degradation created by the ester and ether linkages in the PU. They showed a promising long-term biostability, with excellent resistance to metal ion oxidation, environmental stress cracking and hydrolysis. More recently, silicone has been introduced in the PCU backbone creating silicone copolymers (PCU-S), which have been found to exhibit improved biostability (Elsner et al., 2017).

Property	Silicone	Polyurethane
Elastomeric Properties	Good and Uniform	Excellent
Biocompatibility	Moderate	Excellent
Temperature Resistance	Excellent	Excellent
Biodegradation Resistance	Excellent	Moderate
Oxidation Resistance	Excellent	Moderate

Table 2: List of material properties and characteristics for silicone and polyurethanes for orthopaedic implantation (Christenson et al., 2007; Khan et al., 2005b).

Siebert et al. (2008) show how the Young's Modulus of PCU is very similar to that of cartilage when compared to ultra-high molecular weight polyethylene (UHMWPE). This is beneficial in orthopaedic applications such as the hip and knee joints, where a close match of the Young's Modulus of the materials in contact is essential for the long-term behaviour of the implant. When there is contact between materials with a large mismatch in the Young's Modulus (as in the case of UHMWPE and cartilage), stress transfer to the bone is prevented which could eventually result in bone resorption and implant loosening, in a phenomenon called stress shielding (Aherwar et al., 2016). The stress-strain behaviour of a hyperelastic material such as PCU also comes into play when investigating the material for potential applications in orthopaedics. Mechanical compression tests conducted by Linder-Ganz et al. (2010) revealed that the peak stresses investigated in a PCU meniscal implant were lower than the maximum allowable stress for the material. Similarly, the peak tensile stress was lower than the material's yield strength. Shemesh et al. (2014) conducted other biomechanical tests on the same implant to investigate the strain rate, creep, hysterisis and relaxation measurements in diluted bovine serum, against polyethylene (PE) copies of the femur and tibia. Interestingly, since the implant was effectively a composite of PCU and UHMWPE fibres, the results varied from tests conducted on pure PCU described by Elsner et al. (2015). The stress-strain behaviour for the pure PCU could be described in three phases: (i) Phase I - a linear phase at which the implant exhibited a relatively low Young's Modulus, E, (18 MPa); followed by (ii) Phase II - a non-linear stiffening phase at 20-50 % strain; and finally (iii) Phase III - a linear phase with a lower resistance to strain (10 MPa). However, an increase in the Young's modulus was noted for the composite from Phase I to Phase III (from 3 to 4 MPa). This different behaviour could be attributed to the effects of the reinforcing fibres, which improved the resistance to strain, rather than reducing it.

A series of polyurethanes and polyurethane-ureas of varying degrees of hydrophilicity (they are able to retain water in their structure without dissolving) and hydrophobicity were investigated as candidates for prosthetic replacement of articular cartilage, artificial joint prostheses and percutaneous (beneath the skin) implantable devices (Yoda, 1998). Porous aliphatic polyurethanes were implanted as trials for meniscal reconstruction due to their biodegradable response and were prepared using two different techniques: a) in situ polymerisation; and b) freeze-drying/salt leaching. Results revealed that implants with a macro-porous structure cross-linked with a micro-porous structure showed excellent ingrowth of fibrocartilaginous tissue (de Groot et al., 1990; Elema et al., 1990).

Polyurethane tribological behaviour in a hip joint replacement is dependent on a thin lubricating layer between the articulating surfaces which has to separate the two surfaces under continuous cyclic conditions. Biologically, this is similar to the behaviour exhibited by natural joints as a result of the relative motion created due to the pressure in the synovial fluid and the elastic deformation of the cartilaginous surfaces (Groen et al., 1991). The leading lubrication regime in the tribological behaviour of soft PCU bearing surfaces is composed of a mixture of elastohydrodynamic (EHL) and microelastohydrodynamic (μ-EHL) lubrication systems (Auger et al., 1993; Dowson et al., 1991). The first system occurs when the pressure generated in the lubricating film is sufficient to initiate deformation on any surface so that the articulating surfaces are kept apart. The second system is a localised form of EHL, where the pressure maintains a continuous lubricating film by flattening asperities in the material's surface. Tribological testing conducted by Scholes et al. (2006) on Corethane 80A (medical grade thermoplastic PU), articulating against standard, commercially available femoral heads (CoCrMo and Al_2O_3) exhibited low friction values which were similar to a full fluid-film lubricating regime, with a reported 1% asperity contact. Smith et al. (2000) also reported positive results for friction tests of PU cups (made from a combination of Corethane blends) with respect to typical UHMWPE cups rubbing against CoCrMo femoral heads in 25% calf serum (12.0 ±3.6 mm^3/Mc

vs. 48.2 ±3.7 mm^3/Mc (volume lost per million cycles)). On the other hand, the behaviour of PU in knee joint replacements is dependent on a mixed lubrication regime, however, while it still benefits from a substantial measure of fluid film lubrication, μ-EHL preserves low friction by providing thin, but effective fluid films (Auger et al., 1995; Scholes et al., 2006). Luo et al. (2010) investigated PU as a potential candidate for hemiarthroplasty (replacement of half a joint), instead of the current stainless steel state-of-the-art. Tests on a pendulum friction simulator of PU tibial plates with different elastic moduli (1.4 - 22 MPa) sliding in bovine serum against healthy bovine femoral condyles revealed that PU with lower moduli reduced friction shear and contact stresses, with an observed reduction in the cartilaginous . The higher modulus PU exhibited higher levels of friction shear stresses, however the wear on the cartilage observed was still lower than when stainless steel tibial plates were utilised. This is supported by another study by Pöllänen et al. (2011) who also concluded that PU is more compatible in contact with cartilage than stainless steel.

2.3 Hydrogels

Hydrogels have been on the rise in the last decade as biomaterials due to their excellent biocompatibility and their ability to be manufactured with different properties depending on the application, being biphasic by nature. Although not all hydrogels are elastomeric in nature, hydrogels can be termed as 'elastic polymers' when they exhibit viscoelastic properties. This behaviour is dependent on the groups and linkages making up the structure. As a bulk polymer, hydrogels are normally lacking in the mechanical strength and elasticity required for rigid applications, although some have shown that hydrogels can be be utilised as load-bearing meniscal implants in small animals (Kelly et al., 2007a; Kobayashi et al., 2003). However the main use for hydrogels still remains in coating applications. Medical implants coated with hydrogels have the double advantage of having desirable bulk and surface properties (Yoda, 1998).

Hydrogels are artificial materials consisting of a 3-D structural network which spans across a medium and holds through surface tension. The internal network structure is held together by means of chemical or physical bonding, creating chemical and physical hydrogels respectively. One of the main properties of hydrogels is that they are hydrophilic. The cross-linking of the structure may be either covalent or ionic, with assistance from weaker bonds such as van der Waal forces and hydrogen bonding. Non-cross-linked hydrogels also exist, which are held together by means of crystallites present in the structure, which are insoluble and hence act as physical cross-links. A useful designation for hydrogels being used in the biomedical industry is to divide them as being neutral/non-ionic, anionic, cationic or zwitterionic (Kyomoto et al., 2015). Table 3 refers to some typical hydrogels used in the biomedical industry together with their designation.

Polyvinyl alcohol (PVA) was shown to be functionally and structurally similar to cartilage by Bray et al. (1973). The alcoholic functional group in the structure is responsible for the chemical versatility of the hydrogel, while the hydroxyl groups contribute to its hydrophilic nature. PVA-based hydrogels can be manufactured by forming acetal linkages utilising di-functional cross-linking agents. PVA hydrogels were investigated as coatings in orthopaedic applications due to the similar lubrication and mechanical properties to articular cartilage. Ushio et al. (2003) investigated PVA hydrogels in conjunction with a titanium fiber mesh for a bone fixation arthroplasty in hemi-arthroplasty of the acetabulum. Excellent lubricity was noted at the hydrogel/natural articular cartilage interface.

2-Methacrylolyloxyethyl phosphorylcholine (MPC) was developed by Ishihara et al. (1990) and is a biocompatible polymer which mimics the neutral phospholipids of the cell membranes. These polymers are some of the most biocompatible polymers investigated to date and also exhibit low friction and high lubricity. Arakaki et al. (2010) investigated the effect of a poly (2-acrylamido-2-methylpropane sulfonic acid)/poly(N, N-dimethyl acrylamide) (PAMPS/PDMAAm) double-network hydrogel as a counter-face cartilage in rabbit knee joints. The role

Electric charge	Typical monomer	Hydrophilic group
Nonion	Vinyl alcohol (VA)	$-OH$
	2-Hydroxyethyl methacrylate (HEMA)	$-C_2H_4OH$
Cation	2-(Dimethylamino)ethyl methacrylate (DMAEMA)	$-NR_2H^+$
Anion	Acrylic acid (AA)	$-COO^-$
Zwitterion	2-Methacrylolyloxyethyl phosphorylcholine (MPC)	$-PO_4{}^-(CH_2)_2N^+ \equiv$

Table 3: List of hydrogels with their electric charge and hydrophilic group used in the biomedical industry. Adapted from Kyomoto et al. (2015).

of the implant is to act as an artificial cartilage in defect locations where cartilage degeneration has occurred, mainly due to osteoarthritis. The study revealed that the hydrogel exhibited an extremely low coefficient of friction with respect to the original cartilage, with no detrimental effects on the counter-bearing cartilage.

3 Orthopaedic Implantable Devices using Elastomeric Biomaterials

3.1 Hip Joint Replacement - The TriboFit® Acetabular Buffer - Case Study

Total hip replacements continue to face complications related to osteolysis, wear, fatigue and squeaking. These problems, which are also present in the current state-of-the-art implants, contribute to early implant loosening and premature failure. In 2006, the first instance of polycarbonate urethane (PCU) as a substitute material for hip joint replacements was presented as a commercial cushion-bearing system in the form of an acetabular component, aptly named TriboFit® acetabular buffer (Active Implants, LLC Memphis, TN). The hip replacement consisted of the PCU acetabular intermediary buffer placed between a CoCr femoral head and shell, as shown in Figure 1 (Kelly et al., 2007b).

The purpose of using PCU in the implant was for the material to behave in a similar manner to the natural hip on the acetabular side, with the intention of reducing bone removal during the implantation, by modifying only the acetabulum. Other advantages of using an elastomer as the acetabular component include improved ease of insertion and locking stability of the implant due to a 'snap fit' locking mechanism (Elsner et al., 2017).

In vitro investigations presented by Jennings et al. (2002) on the wear behaviour of the buffer sliding against bone in diluted calf serum (25%) revealed that the wear rate was 2.8 mm^3/Mc after 5 million cycles in a replica of the acetabulum. John et al. (2012) compared wear behaviour of PCU buffers, UHMWPE and cross-linked UHMWPE sliding against cobalt-chrome alloy femoral components. Over 5 million cycles, PCU was reported to have the lowest average material loss (19.1 mm^3/Mc), followed by cross-linked UHMWPE (25 mm^3/Mc) and UHMWPE (100 mm^3/Mc). The large reduction of material loss exhibited by PCU was attributed to the microelastohydrodynamic lubrication (μ-EHL) of PCU in a hemispherical configuration when rubbing against a hard bearing surface. Elsner et al. (2011) have conducted the longest laboratory study on this commercially-available PCU buffer, implanted against a metal shell. After 20 million cycles, the PCU exhibited excellent wear characteristics, with a low particle generation rate (2-3 $x10^6$ particles/Mc) and a steady volumetric wear rate (5.8 - 7.7 mm^3/Mc). The former value is in the order of 6-8 orders of magnitude lower than metal-on-metal bearings and 5-6 orders of magnitude lower than cross-linked UHMWPE. These results were reinforced by profilometry and atomic force microscopy analysis on the PCU buffer after testing, where low damage was observed. One of the most positive conclusions from this study revealed that only 3.4% of the particulates generated by the PCU sliding against the metal were in the range of 0.2 - 10 μm in size, with the large majority of particles being considered as large size (Elsner et al., 2010a). It has been shown that smaller sized particulates often lead to macrophage formation which produce high levels of cytokine tumor necrosis factor (TNF-α), which then leads to osteolysis & aseptic loosening (Keegan et al., 2007; Manley et al., 2008).

Figure 1: TriboFit® Acetabular Buffer (Active Implants, LLC Memphis, TN). Reprinted with permission from Begell House Inc. Publishers from (Kelly et al., 2007b).

Elsner et al. (2017) tested the *in vivo* bio-compatibility and bio-stability of the PCU buffer implant in a sheep model for 6, 12 and 24 months. A variant of the implant having the Co-Cr shell coated with hydroxyapatite was also investigated. In all cases, no functional or gait issues were reported in the sheep and implant. Additionally no gross macroscopic damage in the form of abrasion was observed on the surface of both variants. The hydroxyapatite coated variant exhibited tight fixation of the Co-Cr shell to the acetabulum. The authors attribute the improved fixation to new bone which infiltrated the HA coating. Histological analysis of the retrieved implants revealed that the surrounding tissue did not exhibit any adverse biological response to the implant components, with minimal wear particles being detected.

The TriboFit® Acetabular buffer has been utilised clinically since 2006. In 2013, more than 1200 patients were implanted with the buffer, with the longest implantation time being 7 years (in 2013). By 2017, more

than 1800 patients were utilising the implant with the longest implantation time being 10 years. Wippermann et al. (2008) and Siebert et al. (2008) both analysed retrieved TriboFit® implants at 10.5 and 12 months post-implantation. Both patients experienced hip pain around 8 months after implantation. The average wear rates were found to be 1.5 mm^3/year and 15 mm^3/year respectively. The change in volumetric wear by an order of magnitude after only 1.5 months was attributed to the accumulative effect of debris wear, which considerably increased the wear rate.) According to Wippermann et al. (2008) the average particle size was 2.7 µm (range, 0.5 - 90 µm) by scanning electron microscopy and 0.9 µm by laser diffraction analysis. These values were smaller than those reported in the *in vitro* testing. One of the possible explanations which led to this observation could be that only the particles present in the synovial fluid were analysed, and since smaller particles tend to get dispersed more easily in the synovial fluid, there was a tendency towards a lower particulate size range.

Giannini et al. (2011) conducted a randomised study on the PCU buffer, where they compared the clinical outcomes of 60 osteporotic patients treated for femoral neck fracture, either by means of the TriboFit® PCU buffer or by bipolar hemi-arthroplasty (a surgical procedure which replaces the head of the damaged femur with an implant to stabilize the femur and restore hip function), investigated at 3 and 12 months post-insertion. Interestingly, no statistical differences were observed between the two groups. Additionally, no major adverse complications were reported, and the authors described the procedure to be fast and simple. Another recent study by Moroni et al. (2012) investigated the serum Cr and Co levels in two groups of patients fitted with metal-on-metal total hip arthroplasty and the other with the TriboFit® buffer. A higher metal ion content was observed in the patients fitted with the metal-on-metal implants, where the median levels of Co and Cr were found to be 5.4 and 4.8 times higher respectively than those having the TriboFit® buffer. Additionally, no osteolysis or loosening of the PCU buffer was reported. Elsner et al. (2017) report that until 2017, from 184 implanted PCU buffers, no revision surgeries were required in the patients, up until 5 years follow-up. Currently TriboFit® is the only uncemented acetabular cup with a 0% revision rate after 5 years.

3.2 First Metatarsophalangeal Finger Joint Implants

First metatarsophalangeal joint (great toe) implants are inserted to replace the named joint as an alternative treatment to patients with end-stage arthritis, with the intention of relieving pain and restoring motion (Butterworth et al., 2019; Kawalec, 2017). Utilising metal-based metatarsophalangeal implants results in adverse effects on the region including implant loosening, bone resorption and implant instability. With the introduction of silicone, a single-stem silicone elastomeric implant could be inserted to restore the biomechanical function of the joint, following a resection arthroplasty procedure (Esway et al., 2005; Swanson et al., 1991). However, the adverse wear behaviour of the implant which was rubbing against the natural joint surface was concerning (Esway et al., 2005; Kampner, 1984).

Figure 2: First metatarsophalangeal joint implant with metal grommet. Reprinted with permission from Elsevier from (Esway et al., 2005).

An improved iteration of the implant was created using a constrained double-stemmed silicone elastomeric implant, which had a flexible hinge to replace the head of the first metatarsal and the base of the proximal phalanx (Esway et al., 2005). However, this implant still resulted in failure due to wear and tear caused by the high shear force at the joint, in conjunction with continuous contact of the implant with the sharp edges of the bones (Swanson et al., 1991).

The eventual introduction of metal grommets to the double-stemmed implants, shown in Figure 2, reduced the occurrence of failure, by creating an interface between the bone and the silicone. The first metatarsophalangeal joint implants also act as dynamic spacers, restoring motion to the joint while retaining the alignment and the joint space. However, adverse effects due to degradation have been reported including synovitis, osteolysis and lymphadenopathy caused by particulate debris released from the silicone (Péoc'h et al., 2000; Tang et al., 1995).

3.3 Meniscal Implants

The knee joint comprises of three bones and a complex structure of ligaments and tissue. The bones are the femur, tibia and patella, which are joined together to form a double-jointed structure, namely the patello-femoral and tibio-femoral joints. The tissues include the articular cartilage, synovial membrane and menisci (Affatato, 2015).

The tibio-femoral joint is made up of the femoral condyles articulating against the tibial plateau. The femur's (thigh bone) distal epiphysis is segmented into two condyles, whose geometry remains the most important factor when studying knee stability. The lateral condyle is flatter than the medial, while also being larger, to allow transmission of weight to the tibia, since it is more aligned to the femoral shaft. On the other hand, the medial condyle is narrower, however it has a larger rolling surface, giving it a larger effective articulating area. The femur rubs against the proximal end of the tibia across the tibial plateaus. The superior end of each plateau and the inferior end of the femoral condyles are protected by a layer of hyaline cartilage, which is necessary for skeletal elements to slide and rotate against each other with a low degree of friction, while also allowing for load distribution across the joint (Affatato, 2015).

The menisci, having a complex anatomy, are utilised in a variety of biomechanical functions including load bearing, increasing the contact area of the femur whilst guiding rotation and also in partaking in stabilisation during translation motion. The medial meniscus has a semicircular shape, while the lateral meniscus has a more circular shape, covering a larger area of the tibial plateau (Affatato, 2015; Flandry et al., 2011). Studies focusing on the effect of meniscal tears have revealed that with the loss of meniscal function, there is an increase in degenerative disease, particularly osteoarthritis, possibly due to a change in the load distribution (Englund et al., 2004; Li et al., 2006; Mcdermott et al., 2006). It was also reported that approximately 50% of partial or total meniscectomy patients will suffer from eventual osteoarthritis (Englund et al., 2004). This leads to the notion that the articulating surfaces might be protected by preserving the menisci or by replacing them. Current technology in the field includes tissue engineering in the form of meniscal allografts, which while proven to improve healing and pain relief (Verdonk et al., 2005), still present problems associated with size, rate of disease progression and cost (Cole et al., 2003). There has also been a surge in biodegradable meniscal substitutes made from both synthetic and natural polymers. However these types of materials are generally susceptible to failure under the harsh loading conditions of the knee joint (Kelly et al., 2007a; Kobayashi et al., 2003). Currently the challenge resides in developing synthetic meniscal implants which can withstand the load at the joint, providing a stable biomechanical function, while also being durable and having desirable wear characteristics to function in the knee joint.

Both Kobayashi et al. (2003) and Kelly et al. (2007a) investigated the use of hydrogels as possible meniscal implants to be utilised instead of meniscal allografts. Kobayashi et al. (2003)'s study on rabbits using polyvinyl-alcohol hydrogel (PVA-H) meniscal implants revealed that changes in the articular cartilage was observable after 4-6 months in both meniscectomised (partially removed meniscus by surgery) and implanted knee joints. However, a follow-up after 1 and 2 years revealed that there was little to no subsequent damage after the initial observable degeneration of the implanted joints, while the meniscectomised knees led to more severe damage of the cartilage and even eventual osteophyte formation. Additionally, the implants exhibited good behaviour during implantation, with good wear characteristics and no indication of infection. Kelly et al. (2007a)'s hydrogel-based meniscal implant (Figure 3 (a)) was investigated using an ovine model. The implants, similar to Kobayashi et al. (2003), did not exhibit evidence of permanent deformation or mechanical failure after 2-4 months, in conjunction with no infection observed in the joint of the animal. However, investigation after 1 year of implantation revealed that the hydrogel implant failed in all animals due to a radial tear, which might indicate that the hydrogel composition did not provide the correct mechanical prop-

Figure 3: Implant developed or investigated by: (a) Kelly et al. (2007a) (b) Zur et al. (2011), (c) A. C. T. Vrancken et al. (2017). Reprinted with permission from (a) SAGE publications from (Kelly et al., 2007a); (b) Springer Nature from (Zur et al., 2011) and (c) PLOS ONE from (A. C. T. Vrancken et al., 2017).

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erties for the application. Other sources of failure could have occurred from size mismatch of the implant to the knee joint or due to improper fixation of the implant. In fact, Kobayashi et al. (2003)'s implants were fixed peripherally with sutures with no radial tears, while Kelly et al. (2007a)'s study did not perform this type of fixation.

Studies on Teflon and Dacron meniscal substitutes resulted in failure due to wear-particle induced synovitis (Messner, 1994; Messner et al., 1993).

Li et al. (2006) discuss how the combination of meniscal allografts and polymer scaffolds could improve meniscal regeneration. They observed how reinforced polyglycolic acid (PGA) meniscal scaffolds reacted to cell seeding *in vitro*. The implants were subsequently implanted in New Zealand white rabbits for 36 weeks. They reported that the shape of the scaffold was maintained throughout the duration of implantation, attributed to the reinforcement of the PGA, which resulted in an increase in the compressive modulus by 28 times. They also observed regeneration of fibrocartilage, with an abundance of pretoeglycans, where the presence of collagen in implanted and non-implanted joints was consistent.

The PCU medial meniscus implant (NUsurface® Meniscus Implant, Active Implants Corp.) is a composite elastomeric implant composed of PCU, reinforced circumferentially by UHMWPE. The aim of the matrix is to redistribute the joint loads, while reducing the contact pressure by allowing local material deformation, whilst using the reinforcement to restrain the flow of the elastomer and allow high hoop stresses. The form of the shape was developed to match the shape of the existing cartilaginous surfaces and to fill the joint spaces through magnetic resonance imaging (MRI) (Elsner et al., 2010b). An additional requirement that was considered with this implant included ease of insertion, while allowing the possibility of future joint replacement if needed by not drilling into the bone. *In vitro* investigations on the biomechanical behaviour of the implant on human cadaveric knees were conducted by Linder-Ganz et al. (2010) and Shemesh et al. (2014). The meniscus of the cadavers were removed before implantation, and the investigations were done under compression which was representative of the maximum physiological load attained during gait. The contact pressure distributions on the tibial plateau underneath the implant were found to be similar to the natural knee, suggesting that the PCU implant fulfilled the role of load distribution. Subsequent tests conducted by Shemesh et al. (2014) of static soaking in simulated physiological fluid for 6 months, followed by dynamic fatigue loading of 2 million cycles, showed a slight increase in the implant's width and length around 1 µm, with moderate creep observed. The authors considered the latter effect to be advantageous as this suggested that the implant could conform to changes in the joint morphology, while improving stress distribution. Dynamic fatigue testing described by Elsner et al. (2017) was performed in a knee dynamic simulator for 5 million cycles. The average wear rate was lower than 20 mg/Mc, where the majority of the wear originated during the first 3 million cycles. The creep of the meniscus over time could be the reason for the transient behaviour observed, attributed to an improved lubrication regime. Zur et al. (2011) studied the chondroprotective effects of a variant of the NUsurface Implant (Figure 3 (b)) which was inserted in ewes (female sheep). The implant was composed of (PCU) which was reinforced circumferentially by high modulus Kevlar fibres. The study was conducted on six adult ewes, where the right joint of each ewe served as a control. The material properties and wear response of the implants remained stable after the retention period. Even though histological analysis revealed that there was a slight decrease in the proteoglycan content and cartilage structure, the overall osteoarthritis score (using the Mankin score which is a dedicated evaluation criteria utilised to assess the degree of osteoarthritis) was not different between the control and implanted joints at 3 and 6 months post-surgery. Currently the NUsurface Meniscus Implant is undergoing clinical investigation in the USA, with some promising results, however it is still not approved by the United States Food and Drug Administration (FDA).

An initial study of PCU meniscal implants (Figure 3 (c)) in a goat model were investigated by A. C. Vrancken et al. (2015). However, this implant failed mechanically when the suture came apart in the goat knees during the three-month implantation period. A second study by A. C. T. Vrancken et al. (2017) had the objective of improving the fixation method which failed in the first study by utilising a modified Revo knot, while increasing the implantation period to 12 months. This study also investigated the chondroprotective effect of the implant with respect to control groups comprising of state-of-the-art meniscal allografts, total meniscectomy and a control intact meniscus (6 animals per group). Interestingly, the second study also failed mechanically since the integrity of one of the implants was lost due to a complete tear at the posterior horn extension. Also, in some of the animals, the knot was observed to be partially or totally pulled out of the trans-tibial tunnel, exposing the cartilage. In both studies degenerative changes in the central tibial cartilage was observed across all animals, including the non-operated controls. However, cartilage histopatological conditions were similar across all implants and controls, suggesting that the device was successful in offering sufficient chondroprotection in goat knees with respect to the meniscec-

tomised knee. Additionally, the PCU implant did not exhibit any additional material loss from the 3-month study (A. C. Vrancken et al., 2015), attributed to the nonlinear compressive creep behaviour of the material. A. C. T. Vrancken et al. (2017) hypothesise that the maximum compression of the posterior horn was reached upon 3 months.

4 Conclusions

In this review paper, elastomers used in the development of long-term orthopaedic implants were discussed. Silicones, polyurethanes and hydrogels and their properties were discussed for possible biomedical implantation. Subsequently, the application of these elastomers as orthopaedic implants were reviewed. The following conclusions may be drawn from this review:

- Elastomers including silicone, polyurethane and hydrogels are being investigated as possible material candidates in the development of orthopaedic implants. The combination of their mechanical and biomaterial properties give them a unique edge for possible application in this sector.
- A case study on a PCU acetabular implant utilised in a hip joint replacement revealed that the properties of the elastomer were integral to the behaviour of the implant. Excellent tribological and histological behaviour led to very low revision rates.
- Current studies on meniscal implants lead to the conclusion that although a leap in the development of these implants was observed, long-term studies in animal models still needs to be conducted to ascertain an adequate result on the long-term performance that such implants have on the knee-joint.

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