

Biomaterials in Hip Joint Replacement

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Abstract: Total hip joint replacement is unavoidable in the orthopedic application, for improving the quality of patient life suffering from arthritis. Replacing damaged joint with artificial joint gaining popularity and it became a need in such cases. While joint replacement represents success stories in the field of orthopedic surgery, but maintaining implant for last long is still challenge. The average lifespan of hip joint replacement is about 15 years. Last 50 years research in the field of orthopedics trying to evaluate the biomaterials for hip joint replacement with improved performance in terms of extending joint life. In early days different kind of natural materials like wood, glue, rubber, tissue from living forms and manufactured materials like iron, gold and zinc were used as biomaterials based on trial and error. Biomaterials are such materials which are intended to replace a part or function of the body in reliably economically and physiologically acceptable manner. The aim of this review is to present the overall evaluation of biomaterials mainly developed for a hip joint replacement from early days to current days. In this paper attempt has been made to summarize the evolution of the biomaterial from early days of metals, polymers to present days of ceramics commonly used in the field of orthopedic for hip joint replacement.

Keywords: Hip joint replacement, implant, biomaterials,

1. Introduction

Any disease involving hip/knee joint leads to immense difficulty in walking, and results in severe disability. The hip joint is a spherical joint between the femoral head and the acetabulum in the pelvis (Fig. 1).

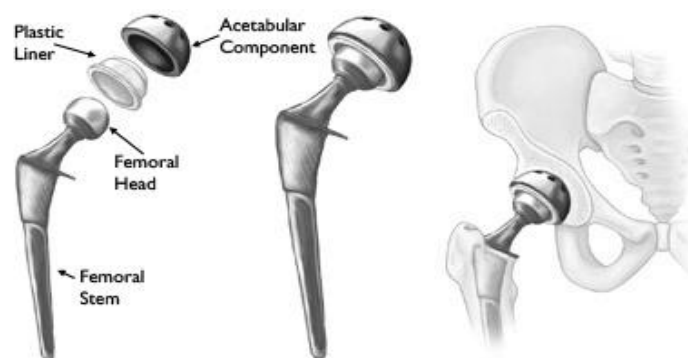


Fig. 1. Components of total hip replacement

Hip joint is ball and socket joint consisting of: 1. Femoral stem, 2. Femoral head and 3. Acetabular component. Fig. 1 shows the components of total hip joint replacement (THR). In the 21st century, medical engineering is an important area of technological development. The design, development and manufacturing of medical implants that replace failed body or organ functions are of great importance for an aging population. Hip replacement is a surgical procedure which replaces the part of damaged hip joint with artificial joint. It is estimated that approximately 250,000 knee replacements and 1 million hip replacements are carried out per year [1]. It is expected that this number will double till 2025 as a result of aging populations worldwide and growing demand for a higher quality of life [2, 3]. Biomaterials are synthetic materials used to develop parts and replace a body part or function of the body part in safe and reliable manner. Biomaterials are used in human body and hence need to be inert and mechanically strong enough to bear the load. Various applications of biomaterials are listed in Table 1.

Table 1. Uses of biomaterials

Sr.No.	Uses of Biomaterials	Example
1	Replacement of damaged or diseased part	Artificial hip/knee joint replacement
2	Improving functionality or abnormality	Cardiac pacemaker
3	Assist in healing	Sutures, bone plates and screws
4	Improving cosmetic abnormality	Mastectomy augmentation, chin augmentation
5	Aid to diagnosis	Probes and Catheters

Biomaterials are expected to work satisfactorily in body environment, where the pH value of body fluid varies from 1 to 9. During daily activities bones are subjected to the stress of about 4MPa and mean load on hip joint is three times the body weight. The peak load on hip joint during jumping time may be up to 10 times body weight; again these stresses are repetitive and fluctuating depending upon activity to be performed [4]. These conditions indicate the situation where biomaterials to sustain and again these conditions vary from patient to patient. Although THR is considered one of the greatest achievement in orthopedic surgery, from an engineering point of view. Hip replacements are not a complete success and still need further development. The main limitation in THR is service life of about 15 years, which is not satisfactory for patients under 60 years of age, about 44% demanding a life expectancy of 20to 25 years [5]. Implant failures can be due to a number of factors, but one of the critical issues is the release of wear particles from bearing surface of the implant. Accumulation of wear particles leads to bone loss and eventually aseptic implant loosening. Therefore it is highly desirable to reduce the generation of wear particles from the implant surface. Infection, wear and breakaway failure are common reasons for revision of THR surgery [6]. To overcome this problem is to develop a material combining wear resistance, biocompatibility and biodegradability. Such material would release less wear particle, which would readily resorb without detrimental effect to tissue or bone. The first attempt of hip joint replacement was reported in early 1890 by using ivory and stainless steel. In 1962, Sir Charnley developed a cemented stem with a 22.22mm head in stainless steel combined with a cup made of Ultra High Molecular Weight Polyethylene (UHMWPE) [7]. The first metal-on-metal (CoCr-CoCr) total hip replacement (THR) was unsatisfactory in terms of high friction forces and high rate of wear. Titanium alloys and stainless steel are also frequently used in THR, but the main risk with use of metal alloy implants is the release of metal ions due to wear and creating a negative effect like aseptic loosening caused by adverse biological reactions due to wear products. Therefore metal-on-UHMWPE bearing became advantages or preferable to the metal-on-metal system. A lot of literature from hip simulator studies proved improvement in wear resistance of cross-linked UHMWPE [8, 9]. Since from last four decades bio-inert alumina ceramic (aluminum oxide) have presented an attractive

alternative for THR bearing surface in terms of improved wear resistance and extended joint life. Nowadays THR is not only applicable to elder generation, but it is introduced in younger generation also, which are subjected more movement compared to the old generation. So extending the life span of THR is still needs more attention. The goal of developing alternative THR material is to create joint with decreased friction and wear rates but with increased strength.

2. Total Hip Joint Replacement Materials

2.1 Metallic Materials

In the twentieth-century stainless steel and cobalt–chrome-based alloys were successfully used in orthopedic applications. Fig. 2 shows metallic implant.



Fig. 2. Metallic hip implant

Stainless steel materials are more resistant to a broad range of corrosive environment due to high Cr content (more than 12 wt %) of steel, it allows the formation of a firmly adherent, self-healing and corrosion resistant coating oxide of Cr_2O_3 . Despite these properties stainless steel implants are degraded because of pitting, crevice, corrosion fatigue, fretting corrosion, stress corrosion cracking, and galvanic corrosion in the body [10]. The wear resistance of austenitic stainless steel is relatively weak. Generation of a large amount of wear debris leads to aseptic loosening of joint. Moreover the modulus of stainless steel is about 200 GPa which is much higher than that of bone. Cobalt-chromium alloys can be classified into two types;

1. The Co-Cr-Mo alloy (which is usually used to cast a product), castable Co-Cr-Mo alloy has been used in dentistry for a long time and currently in making artificial joints
2. The Co-Ni-Cr-Mo alloy, (which is usually wrought by hot forging), wrought Co-Ni-Cr-Mo alloy is a comparatively new material which is now used for preparing the stems for the prosthesis of heavily loaded joints such as the knee and hip.

Added advantage of cobalt-based alloys is high corrosion resistant even in chloride environment due to the formation of oxide layer within the human body environment [11, 12, 13 and 14]. They have superior mechanical properties such as high resistance to fatigue and cracking caused by corrosion with an excellent wear resistance. Although these materials have a high elastic modulus (220–230 GPa), which greater than that of cortical bone (20–30 GPa) [9]. But due to corrosive environment in the human body the elements such as Ni, Cr and Co are found to be released from the stainless steel and cobalt chromium alloys [11]. The corrosion products of Co-Cr-Mo are more toxic than those of stainless steel.

Titanium based alloys are also popular in THR, because of its characteristics like low density (approx. 4700 Kg/m^3), high specific strength, good resistance to corrosion due to the formation of an adhesive TiO_2 oxide layer and complete inertness along with biocompatibility. Moderate elastic modulus of approximately 110 GPa, which is only half of that of surgical stainless steel or cobalt-based alloys and five times that of cortical bone, leads to more physiologically sound stress distribution in the implant bone. The intermediate layer of cement does not require in Ti implants, which require in case of stainless steel and Cobalt-

chromium alloys. Ti and Ti alloys are wear resistant due low shear resistance. Two Ti-based alloys are available for implants are commercially pure Ti and Ti–6Al–4V, but due its excellent mechanical strength Ti-6Al-V4 is replacing commercially pure Ti [15]. Long-term use of Ti alloys creates health problem like Alzheimer disease and neuropathy, which mainly arises due to the release of aluminum and vanadium [16]. Although vanadium is an essential element in the human body, the excess level is toxic and it may aggravate when implant fractures. In 1967 Buehler & Wang [17] investigated NiTi alloys, working on shape memory effect. Shape memory alloys are more suitable than metallic materials in load- bearing applications, due to the ability to deliver uniform compressive stress after recovery of pre-strain upon heating. The serious issue associated with NiTi alloys is the release of Ni ions, which are allergic, toxic and potentially carcinogenicity. To overcome this problem Nb-based materials are under development. Table 1 summarizes the properties of various metallic materials used for THR.

Table 2. Mechanical properties of metal implants and human bone [16]

Material	Tensile strength MN/m ²	Yield strength MN/m ²	Elongation at fracture	Vickers hardness (Hv)	Young's modulus GN/m ²	Fatigue limit GN/m ²
316l SS(annealed)	650	280	45	190	211	0.28
Wrought						
Co-Cr alloy	1540	1050	9	450	541	0.49
Cast Co-Cr alloy	690	290	8	300	241	0.30
Titanium	710	270	30	-	121	0.30
Ti-6Al-4V	1000	970	12	-	121	-
Human bone	137.3	-	1.49	26.3	30	-

2.2 Polymer Materials

Table 3. Mechanical properties of polymer implants [21]

Material	Modulus (Gpa)	Tensile strength (Mpa)
Polyethylene (PE)	0.88	35
Polyurethane (PU)	0.02	35
Polytetrafluoroethylene (PTFE)	0.5	27.5
Polyacetal (PA)	2.1	67
Polymethylmethacrylate (PMMA)	2.55	59
Polyethylene terephthalate (PET)	2.85	61
Polyether ketone (PEEK)	8.3	139
Silicone rubber (SR)	0.008	7.6
Polysulfone (PS)	2.65	75

In 1962 Sir John Charnley, introduced metal-on-polyethylene hip prostheses along self-polymerizing polymethyl-methacrylate (PMMA) bone cement for fixation [7]. Use of bone cement fixation with a metal stem, and a polished femoral head articulating on an ultra-high molecular weight polyethylene (UHMWPE), proposed by Charnley became the standard for THR [18, 19] and was further adapted for knee joint replacement also in the 1960s to 70s. Polymer materials are popular for various applications due to their low cost, a wide range of mechanical and physical properties. Polymers are divided into two categories according to their durability in biological environments: 1. Biostable and 2.Biodegradable [20]. Examples of biostable polymers are polyethylene (PE), poly (methylmethacrylate) (PMMA) and polyetheretherketone

(PEEK) which are used in hip and dental implants. Ultrahigh molecular weight polyethylene (UHMWPE) has also been used extensively for hip and knee joints [4, 21]. The second class of biodegradable polymers is poly (ε-caprolactone) (PCL), poly (glycolic acid) (PGA), poly (lactic acid) (PLA) and poly lactic-co-glycolic acid (PLGA), which can break down gradually in the physiological environment of the body into biocompatible products [22]. From early research it found that UHMWPE is an acceptable polymer in THR. Table 3 presents mechanical properties of polymer implants.

2.2.1 Composite polymer

While working implant and bone are unevenly loaded, which is called as ‘stress shielding’ or ‘stress protection’? In such cases low modulus material like polymer are suitable [19], but low modulus associated with little strength restricts the potential use of polymers. While Performance of UHMWPE is satisfactory for the short term, but for long term application researcher suggested reinforcing of UHMWPE with carbon fibers [23] to improve its creep resistance, stiffness and strength. Reinforcing PEEK with carbon fiber offers superior wear resistance as compared to unfilled UHMWPE when rubbed against either metal or ceramic [24, 25]. Carbon fiber/Ultra-high molecular weight polyethylene (CF/UHMWPE), Carbon fiber/epoxy (CF/epoxy) and CF/PEEK are certain examples of composite polymer. One of the serious problems associated with THR is a mismatch of the stiffness of femur bone and prosthesis. In the commercial hip joint stems are made of metal alloys, which are 5 to 6 times stiffer than bone. This mismatch of stiffness leads to aseptic loosening and failure of joint [19]. This implant loosening and failure could be reduced with improved prosthesis design and using a less stiff material with mechanical properties similar to bone. With the requirement of high strength for hip prosthesis design, polymer composite offers good strength comparable to metal and more flexibility than metal. The advantage of composite polymer is that it can provide tailor implant with selecting material ingredients and controlling ingredient composition, which helps to manage strength and modulus according to requirement. CF/epoxy stems prepared by Chang et.al. [26] by laminating 120 layers of unidirectional piles in a predetermined orientation and stacking. CF/PEEK composite stem (Fig. 3) possess a mechanical behavior similar to that of femur [27].

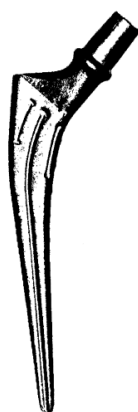


Fig. 3. An injection molded CF/PEEK composite stem for THR

Further reinforcing of UHMWPE presented addition of multi-walled carbon nanotube. Ruan S.L. et.al [28] mixed chemically treated multi-walled carbon nanotubes (MWCNT) with UHMWPE using ball mill and found that an addition of 1% weight of MWCNT revealed an increase of 150% in strain energy density, 140% in ductility and up to 25% in tensile strength compared to pure UHMWPE. Reinforcement of UHMWPE by adding MWCNT allows the improvement of mechanical characteristics and superior wear behavior (decreased wear volume and wear coefficient) [29] compared to that of UHMWPE. However few animal

studies have observed the adverse effects of MWCNT on the lung, liver, and renal.

2.2.2 Highly cross-linked UHMWPE

In total hip replacement system typically applies ultra-high-molecular-weight polyethylene (UHMWPE) insert that articulates against a cobalt-chromium alloy or ceramic to restore the function of a damaged joint. Although properties of the composite polymer are suitable for THR there is no appreciable difference in wear rate of reinforced and unreinforced UHMWPE [30], the effect of carbon fiber reinforcing on wear characteristic of UHMWPE is unclear. The detrimental debris, generated due to abrasive/adhesive wear of UHMWPE causes periprosthetic osteolysis and results in THR failure. In the late 1990s with improving the wear resistance of UHMWPE, crosslinked and thermally treated UHMWPE developed for THR, the so-called first-generation highly cross-linked polyethylene (HXLPE) [31]. Cross-linking UHMWPE can be achieved by generating free radicals along the backbone of the long chains that make up the polyethylene molecules. The free radicals produced in adjacent chains combine with each other, forming carbon-carbon covalent bonds, which are the so-called cross-links. The cross-linking can be achieved by exposing the polymer to ionizing radiations. The methods included cross-linking polyethylene with high dose (1000 kGy or 100 Mrad) gamma radiation in the air [32], gamma radiation (100 kGy) in the presence of acetylene [33], and silane chemistry [31]. But gamma irradiation of cross-linking of polyethylene leads to formation oxidation products and free radicals causing scission and decrease in molecular weight of polyethylene, reducing its mechanical properties and accelerating wear. According to the irradiation dosage and the method of free radical stabilization there are various products of HXLPE. Nowadays, radiation chemistry is the preferred method of cross-linking and neither peroxide nor silane chemistry is used. Post-irradiation thermal treatment steps are employed to reduce the concentration of free radicals and improve the long-term oxidative stability. There are several commercially available contemporary approaches for improving the wear and oxidation resistance of polyethylene by radiation chemistry for applications in THR. Extensive data from hip joint simulator studies shown improvement of wear resistance of these HXLPE [34, 35]. Low wear of HXLPE permitted the use of larger diameter femoral head, allowing a greater range of motion and enhanced activities with a wider range of motion, inherent errors in acetabular placement provides safety [36].

2.3 Ceramic Material

In late 18th century, the controlled implantation of bioceramic started in dental with the use of Plaster of Paris, or gypsum for bone filling. Ceramic bearings were first introduced as alternatives to polyethylene (PE) bearings in THR about a decade after Sir John Charnley introduced the first durable THR with a metal-PE articulation. In 1965, the first alumina (Al_2O_3) material dedicated for hip joint was patented [37]. Pioneering application of bioceramic was replacing traditional metallic femoral heads of hip prostheses using high density and pure alumina [38]. Ceramic are a crystalline structure where atoms are held together by the ionic and covalent bond. This ionic bonding gives these compound high compressive strength, hardness and chemical inertness. Alumina and zirconia (ZrO_2) are oxidized ceramics; their high oxidation level renders them chemically inert, resistant to corrosion and stable over the long term. Alumina is commonly used ceramic for THR owing to its low friction and wear coefficient, makes its suitable alternative for the orthopedic bearing. Comparative to alumina, zirconia offers 2 to 3 times more flexure strength and fracture toughness and thus it is most fracture resistant ceramic. Alumina leads to catastrophic failure; to avoid this risk zirconia was introduced to replace alumina with superior wear resistance. Poor fracture toughness of alumina leads to the release of wear particles. Pure zirconia is unstable and it transforms from one form to another, leading to change in shape and volume. To avoid this zirconia is added with stabilizing material like magnesia (magnesium oxide), quicklime (calcium oxide) and yttria (yttrium

oxide). Controlled phase transformation is used to develop different zirconia composite for orthopedic application such as:

1. Tetragonal zirconia polycrystal (TZP): is strongest and toughest zirconia based ceramic, with optimal material density and fine grain size.
2. Yttria stabilizing TZP (Y-TZP): suitable with PE or XLPE and it became an attractive alternative to alumina as structural ceramic because of its higher fracture toughness and strength. But it is prone to low-temperature degradation (aging) in the presence of water [39]. Aging occurs due to the transformation of tetragonal to monoclinic at the surface triggered by water molecules, results in surface roughening, which impact on wear rate, as roughening increases wear rate.

2.3.1 Alumina-zirconia composites

Mixed composite of ZrO_2 and Al_2O_3 are also used in hip replacement, these materials are known as 'zirconia- toughened alumina (ZTA)', has shown success THR [40]. ZTA is 2 phase material made of zirconia particles dispersed in a dense, fine-grained alumina matrix. It has a hardness of alumina, with improved strength and toughness. But ZTA is still unstable, as it derives its strength and toughness from the mechanism that resulted in catastrophic failure of the ZrO_2 – based orthopedic material [41]. ZTA achieve their properties through phase instability of material itself. But this material instability is exacerbated by temperature and moist environment (i.e. condition found in the human body). As material transforms it lose its strength and toughness and over time it is no stronger than conventional alumina.

2.3.2 Nonoxide ceramic- silicon nitride

Silicon Nitride (Si_3N_4) and silicon carbide (SiC) are nonoxide ceramics. Silicon carbide has increased strength and hardness with fracture toughness similar to alumina. Again its corrosion and wear behavior in the physiological environment is unclear. Silicon nitride is biocompatible with high fracture toughness and more resistant to crack propagation than alumina [42, 43]. During last 60 years silicon nitride is used in various industrial applications due to its intrinsic material properties, make it suitable for articulation against bearing steel in the hybrid bearing. Silicon nitride used in rolling contact application due its low density (half that of bearing steel), low friction, corrosion resistance and reliable under extreme conditions in a space vehicle and aircraft [44]. Silicon nitride shows favorable biocompatibility along with cell adhesion. Silicon nitride is implanted in spinal surgery for last four years without any adverse effect. Xu J. et.al. [45] investigated wear performance of silicon nitride sliding against itself in water showing the low coefficient of friction and low wear. The wear of silicon nitride in water occurs mainly due to the tribochemical dissolution of material without the release of the solid particle. Boshitskaya et.al. [46] presented that silicon nitride powder dissolve in blood serum, gastric juice and a synthetic biochemical media at pH 7.4, suggesting the use of silicon nitride for hip joint replacement with less wear and those produced wear particles would be biodegradable. Silicon nitride sliding against silicon nitride in the presence of bovine serum and PBS found the formation of tribofilm on surface controlling coefficient of friction and wear rate [47]. Considering orthopedic application improved the coefficient of friction and low wear rate of silicon nitride are confirmed and advantages over CoCr alloy [48]. During testing with an increase in sliding distance silicon nitride contact surface becomes smooth due to tribo-chemical polishing and results in low friction [49]. Ability to be formulated into porous substrate and a hard bearing surface makes silicon nitride best alternative in orthopedic and THR materials list. Silicon nitride prepared by situ toughening has mechanical properties (Table 4) which are superior to alumina and based composites currently used for THR. Silicon nitride sliding against silicon nitride or CoCr alloy has lowest wear rate comparable to alumina sliding against alumina bearing [50]. Fig. 4 shows silicon nitride based implants developed by Amedica Corp. USA.

Table 4. Properties of in situ toughening silicon nitride in comparison to Al₂O₃, ZrO₂-toughened Al₂O₃ (ZTA), Y₂O₃-stabilised ZrO₂ (YSZ) and CoCr [50] (at room temperature)

Property	Si ₃ N ₄	Al ₂ O ₃	ZTA ^a	YSZ ^b	CoCr	PEEK	Ti alloy	Cortical bone*
Density (gm/cm ³)	3.15-3.26	3.986	4.37	6.04	~8.5	1.29	4.43	1.85
Elastic modulus (GPa)	300-320	400-450	350	210	210-250	4.2	105-115	8-12
Poisson's ratio	0.25-0.27	0.27	0.24	0.30	0.27-0.32	0.36	0.34	0.6
Tensile strength (MPa)	350-400	250-300	-	-	-	10-110	920-980	50-130
Compressive strength (MPa)	2500-3000	2000-3000	2400	2200	600-800	130-140	950-990	130-190
Flexural	800-1100	300-500	1000	1050	-	160-180	-	-
Fracture toughness MPa m ^{1/2}	8-11	4-5	5.7	10.5	50-100	-	75	-
Vickers Hardness (GPa)	13-16	14-16	19.1	12.5	3-4	-	3.4	-
Thermal expansion coefficient (10 ⁻⁶ /k) (25-1000°C)	3.0-3.5	8.0-8.5	8.0-8.5	11	~14	47	8.6-9.6	-
Thermal conductivity (W/m-k)	30-40	30	30	1.8-2.9	~100	-	6.7	-
Surface composition	SiNH ₂ and SiOH groups	Al ₂ O ₃	Al ₂ O ₃ /ZrO ₂	ZrO ₂	CoO/Cr ₂ O ₃	OH groups	TiO ₂ /Al ₂ O ₃	-
Isoelectric point	9	8-9	8-9	7.5	-	-	-	-
Surface charge at pH=7	Lightly positive	Slightly positive	Slightly positive	Slightly positive	-	-	-	-

^a 20 Vol% ZrO₂.

^b 3 mol% Y₂O₃

*Properties of cortical bone are shown for reference.



Fig. 4. Silicon nitride based spinal and orthopedic implants-courtesy Amedica Corp. USA.

Boron compounds are widely used in a tribological application like friction modifier, antioxidant, antiwear additives with the advantage of environmentally friendly. It is also a very favorable element for coatings and thin films in the biotribological and biomedical application. Anabtawi et.al. [51] evaluated the biocompatibility of boron coatings and Klepper et.al. [52] presented tribomechanical properties of thin boron coatings on cobalt alloy in an orthopedic application with no loss of coating during the test. They concluded that thin coating of boron on Co-Cr-Mo surface could prolong the life of Co-Cr-Mo – UHMWPE contact in the hip joint. The lubrication properties of h-boron nitride are comparable to those of phospholipids, which are the best lubricant in human [53]. Boron is a very hard material and provides lubricity with boric acid when boron oxide formed in a moist environment. The addition of boron nitride in non-oxide ceramic may present a good alternative for joint replacement material.

3. Conclusion

The basic aim of developing alternative THR materials is to create a joint with low friction and wear rate with increased strength. There is continuous development of material from early days of metals to nowadays nonoxide ceramic. Every material has its advantages and disadvantages that must be considered during application. Metal on metal and alumina on alumina-based joints are best in tribological view. While HXPLE has shown excellent wear resistant with better shock absorption. Development of ceramic material to nowadays silicon nitride has presented a very good alternative for hip joint replacement. The ideal THR material is still needed to be evaluated with the modifying metal surface, improving the polyethylene and developing composite ceramic. Coating or addition of boron nitride in nonoxide ceramic like silicon nitride implant material also presents the opportunity of development of future material.

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