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分担研究報告書

関節摺動面の安定性の検討

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研究要旨：人工股関節手術後に高齢者の歩行能力を回復させ、将来の寝たきりを予防するには、訓練を早期に開始しなければならない。このためには、人工股関節の特性として、脱臼をしない安定性と、弱い筋力でも可動域を獲得できるという性能が必要である。

われわれは、生体の関節軟骨表面で数十年にわたり潤滑性の改善に寄与している、ナノメーターオーダーのリン脂質層に着目し、生体適合性と潤滑特性に優れた 2-methacryloyloxyethyl phosphorylcholine (MPC) ポリマーでライナー表面にナノレベルの処理を加える、長寿命型の人工股関節を創出した。

本研究の目的は、関節摺動面の安定性・吸着性を向上するため、人工股関節のインプラントの形状を改良することである。このため、今年度は、大腿骨コンポーネントの頚部が寛骨臼コンポーネントの周縁部に接触するまでの関節可動域を指標として、（1）骨董径が与える影響を算出した。続いて、下肢の自重によって骨頭が引き下げられライナー面から離れる「浮き上がり防止」については、ライナー摺動面—骨頭間の吸着力を指標として、ライナー面の Poly (MPC) (PMPC) 処理が与える影響—を検討した。関節摺動面の安定性のための関節可動域の増大には、関節面を構成する骨頭部分の大径化が有効であることが確認された。また、関節摺動面の吸着性を向上するために、MPC ポリマーを用いた処理は有効である可能性が示唆された。次年度以降は、このモデルを使用し、臼蓋コンポーネント、ライナー、大腿骨コンポーネント等、インプラントのデザインに改良を加え、関節摺動面の安定性・吸着性を向上する新しい人工股関節の形状を検討する予定である。

A．研究目的

人工関節手術は、変形性関節症や関節リウマチなど疾患または外傷などにより喪失した関節の機能を再建する優れた治療法であり、我が国で年間約 13 万件の手術が行われている。高齢化が進む我が国において、高齢者の寝たきり予防に対する人工関節が果たす役割は益々大きくなっている。

人工股関節手術後に高齢者の歩行能力を回復させ、将来の寝たきりを予防するには、訓練を早期に開始しなければならない。しかし、高齢者は筋力低下していて関節を支持する力が弱く、脱臼の危険性が高い。また、このことは関節の可動域の獲得も困難にしている。言い換え

れば、人工股関節を入れた高齢者が将来寝たきりになるのを予防するには、人工股関節の特性として、脱臼をしない安定性と、弱い筋力でも可動域を獲得できるという性能が必要である。

この問題の解決に、関節面を構成する骨頭部分の大径化が有効であることは諸家が報告している。しかし体格の小さな日本人では、骨頭を大径化するには、対向して関節面を構成するポリエチレンライナーを相当に薄くせざるを得ない。また、大径化による接触面積の増加は、人工股関節の弛みの主因となる摩耗粉の産生増加の原因となる。この結果、現行の耐摩耗性では短期間に入れ換えの手術が必要になる可能性が高い。したがって、関節面の耐摩耗性、生体適合性、安定性を同時に達成することができる人工股関節が求められている。

われわれは、長寿科学総合研究事業、臨床応用基盤研究事業を通じて、耐摩耗性と生体適合性を両立した長寿命型人工股関節を創出した。この人工股関節は、生体の関節軟骨表面で数十年にわたり潤滑性の改善に寄与している、ナノメーターオーダーのリン脂質層に着目して創出したもので、10～15年といわれる人工股関節の寿命を飛躍的に延長させる目的で、生体適合性と潤滑特性に優れた 2-methacryloyloxyethyl phosphorylcholine (MPC) ポリマーでライナー表面にナノレベルの処理を加える、独自の新技術を用いたものである。平成19年から東京大学医学部附属病院などで治験が開始されている。本研究の目的は、この技術の新たな可能性に着目し、さらに安定性に優れ、高齢者の寝たきり予防に役立つ革新的な人工股関節を開発することである。

昨年度の成果を踏まえ計画を点検した。臨床で困っていることは、順調に機能している人工股関節が何かの拍子ではずれ、使用者が強い痛みを感じて歩けなくなることである。医師は、患者が述べる脱臼寸前の身体の動きおよび整復時の所見に基づいて、脱臼に至った機転を推定するが、必ずしも特定できない。われわれは、今年度の研究にあたり、脱臼の機転を「衝突＋回転」、「衝突＋破壊」、「浮き上がり」の3つに整理した。ここでいう衝突とは、関節運動の極において大腿骨コンポーネントの頚部が寛骨臼コンポーネントの周縁部に接触し、そこが梃子の支点となって骨頭がライナー面から離れる現象を指す。

離れるだけであれば、逆方向の関節運動によって骨頭がライナー面に還納される。人工股関節使用者の中に、座位での体動時などに「はずれるような変な感じ」があると訴える例があり、骨頭がライナー面から離れ支持性を失った感覚を述べているのかもしれない。これに対し、離れた状態で回転が加わり骨頭がライナーの外に移動すると、逆方向の関節運動によって脱臼が成立する。また、ライナー素材によっては衝突によって破損することがあり、脱臼に至ることが報告されている。最後の「浮き上がり」は下肢の自重によって骨頭が引き下げられライナー面から離れる現象を指す。この事象が立体遊脚期に起きた場合には、足部の設置で骨頭はライナー面に還納される可能性が高い。しかし、坐座で起きた場合には、立ち上がり動作で脱臼が成立する可能性がある。筋電図を用いた生理学的研究において、安静時に大腰筋や中殿筋などの股関節周囲筋から電気活動が記録されていない事実はこの推定と矛盾しない。以上の検討から、今年度の研究計画「(a)抗脱臼機構および関節稼動領域の検討、(b)コンポーネント形状の改良」において、「衝突の回避」、「浮き上がりの防止」という2つの課題を追求することにした。

第一に「衝突の回避」については、衝突までの関節可動域を指標として、

（1）骨董径が与える影響を算出した。第二に「浮き上がり防止」については、ライナー摺動面—骨頭間の吸着力を指標として（2）架橋ポリエチレン（CLPE）と金属骨頭での標準値、（3）ライナー面の Poly（MPC）（PMPC）処理が与える影響—を検討した。

B．研究方法

1．PMPC 処理 CLPE の作製

ベンゾフェノンおよびアセトンは、和光純薬製を用いた。MPC モノマーは、日油製を用いた。PE 基材には、人工股関節に使用されている CLPE を用いた。

CLPE 試験体を 10 g/L に調製したベンゾフェノン含有アセトン溶液に 30 秒間浸漬した後、速やかに引き上げた。室温にて試験体表面のアセトン溶媒を除去した。完全に脱気した純水を用いて、MPC 水溶液（0.5 mol/L）を調製した。ベンゾフェノンを表面にコーティングした CLPE 試験体を、MPC 水溶液に浸漬し、5 mW/cm2 の紫外線（中心波長 350 nm）を 90 分間照射することでグラフト重合を行った。照射中、MPC 水溶液を 60℃になるよう調整した（図 1）。重合後、CLPE 試験体を超純水およびエタノールにて十分に洗浄し、PMPC 処理 CLPE を得た。

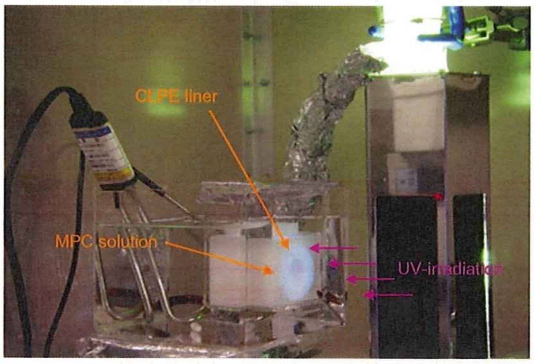

図 1．PMPC 処理装置

2．関節可動域の計算

日本メディカルマテリアル株式会社製ライナー（K-MAX Q5 ライナー）、骨頭（K-MAX HH-02 ボール）、およびステムネック（K-MAX 9 mm ネック）デザインを用いて、コンピューター支援設計（CAD）システムにより関節可動域の計算を行った。

3．引き抜き試験

引き抜き試験には、内径 26 mm の日本メディカルマテリアル株式会社製 CLPE（CLQC）ライナー、PMPC 処理 CLPE ライナー（CLQC を MPC 処理したもの）、および骨頭径 26 mm の日本メディカルマテリアル株式会社製コバルトクロム（Co-Cr）合金骨頭（K-MAX HH-02）を、各々3 セット準備した。

インストロン万能試験機（5600R1）を用い、Co-Cr 合金骨頭を軸方向に引き抜く際に生じる抗力（吸着力）により評価した（図 2）。

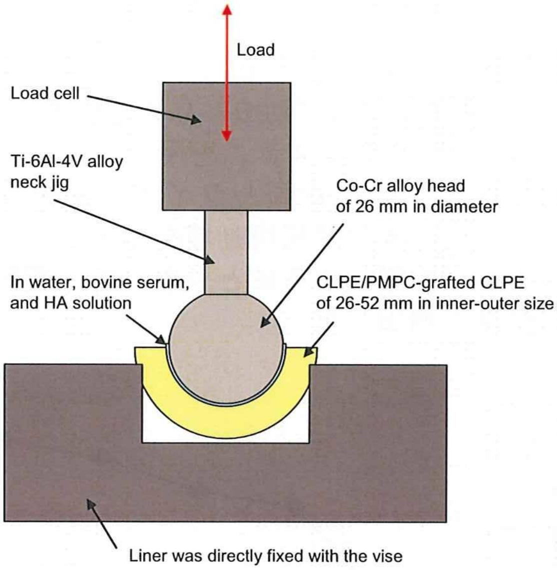

図 2-1．引き抜き試験模式図

初期荷重（50 kgf）を、関節摺動面に加えた後（10 秒ほど静止させた後）、5～500 mm/min の離れ速度で骨頭を引き抜き、その吸着力を測定した。各条件につき、3 回の試験を行った。試験環境（摺

動面）には、蒸留水および 27%ウシ血清を用い、室温にて試験をおこなった。

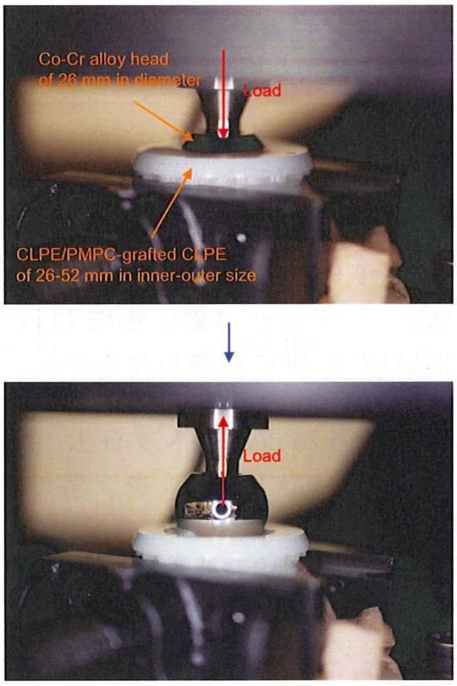

図 2-2. 引き抜き試験の様子

C．研究結果

1. 骨頭径が関節可動域に与える影響

図 3 に、CAD システムを用いて、種々の骨頭径をもつ骨頭とライナーを組み合わせたときの関節可動域を示す。

骨頭径が増加するにともなって、関節可動域も増加した。

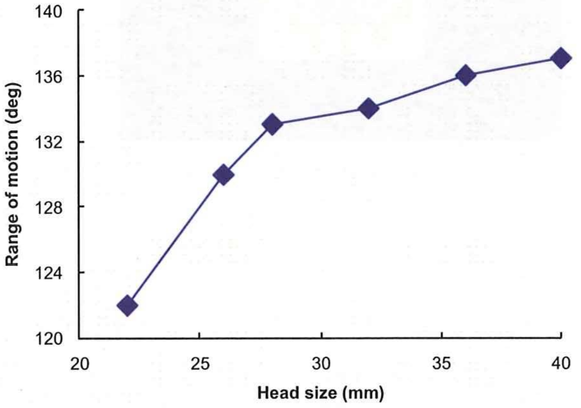

図 3-1. 引き抜き試験模式図

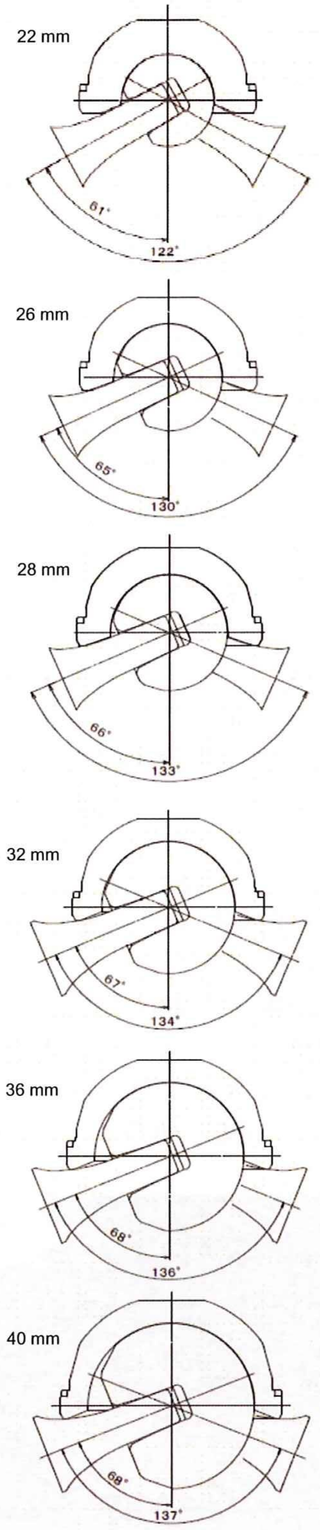

図 3-2. 種々の骨頭径をもつ骨頭とライナーを組み合わせたときの関節可動域

2. 引き抜き試験

図 3 に、CLPE および PMPC 処理 CLPE ライナーと Co-Cr 骨頭との摺動面の吸着力の測定結果を示す。

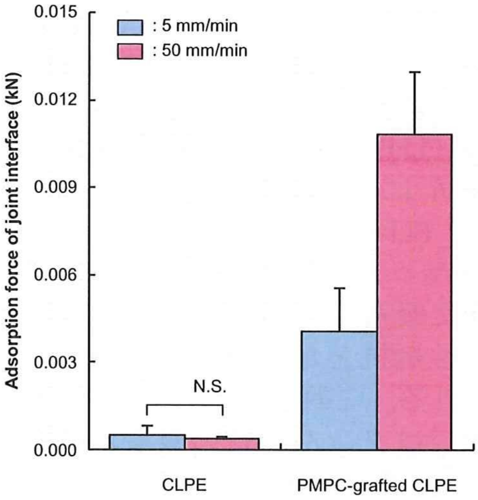

図 3. CLPE および PMPC 処理 CLPE ライナーと Co-Cr 骨頭との摺動面の吸着力

5 mm/min、50 mm/min のいずれの速度で骨頭を引き抜いたときも、PMPC 処理 CLPE ライナーと骨頭の吸着力は、CLPE ライナーと骨頭のそれに比べ高い値となった。蒸留水環境下において、離れ速度が 5 mm/min から 50 mm/min に増加したとき、CLPE ライナーの吸着力は変化しなかったが、PMPC 処理 CLPE のそれは大きく増加した。

図 4 に、種々の潤滑液環境において、離れ速度を変化させたときの CLPE および PMPC 処理 CLPE ライナーと Co-Cr 骨頭との摺動面の吸着力の測定結果を示す。

蒸留水環境下において、CLPE の吸着力は、離れ速度に関わらず 0.0005～0.0041 kN と低い値を示した(図 4-1)。これに対し、PMPC 処理 CLPE ライナーのそれは、離れ速度が 5 mm/min から 100 mm/min に増加するにともなって 0.0114 kN にまで増加したが、その後、200 mm/min 以上の離れ速度では徐々に低下した。蒸留水環境下において、50～100 mm/min の速度で骨頭を引き抜いたとき、PMPC 処理 CLPE ライナーと骨頭の吸着力は、CLPE ライナーと骨頭のそれに比べ 2.6～8.8 倍と高い値を示した。

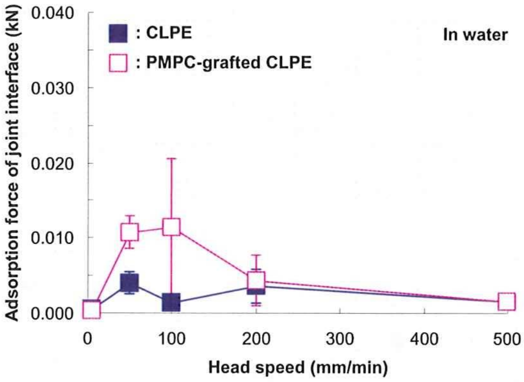

図 4-1. 蒸留水環境下における CLPE および PMPC 処理 CLPE ライナーと Co-Cr 骨頭との摺動面における吸着力

ウシ血清環境下では、離れ速度が 5～200 mm/min の範囲において、CLPE および PMPC 処理 CLPE ライナーの吸着力は低い値（0.0003～0.0024 kN）でほぼ一定であった(図 4-2)。その後、MPC 処理 CLPE の吸着力は離れ速度が 500 mm/min に増加しても変化なかったのに対し、CLPE ライナーのそれは 0.0088 kN にまで増加した。

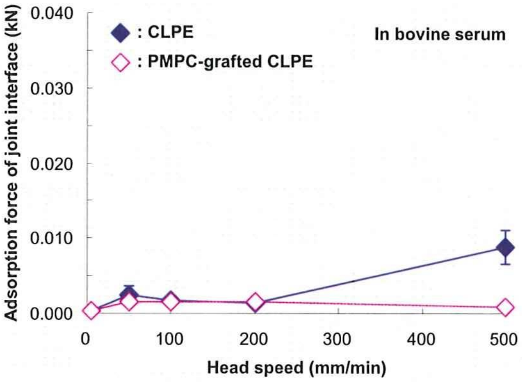

図 4-2. ウシ血清環境下における CLPE および PMPC 処理 CLPE ライナーと Co-Cr 骨頭との摺動面における吸着力

ヒアルロン酸製剤環境下では、離れ速度が 5 mm/min から 50 mm/min に増加するにともなって CLPE および PMPC 処理 CLPE ライナーの吸着力は、各々0.0297 kN、0.0323 kN にまで増加したが、その後、500 mm/min 以上の離れ速度では徐々に低下した(図 4-3)。ヒアルロン酸製剤環境下で得られた吸着力はいずれも、水およびウシ血清環境下で得られたそれらに比べ、高い値を示した。

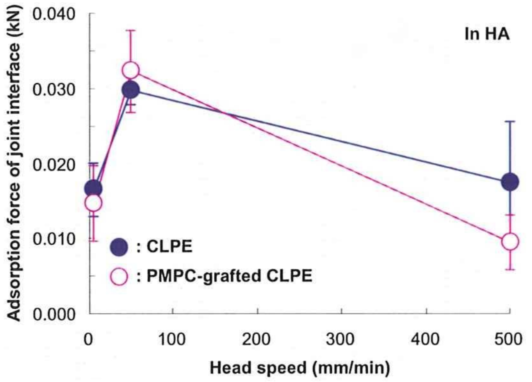

図 4-1. ヒアルロン酸製剤環境下における CLPE および PMPC 処理 CLPE ライナーと Co-Cr 骨頭との摺動面における吸着力

D. 考察

本研究において、人工股関節における摺動面の安定性の検討として、下肢の自重によって骨頭が引き下げられ、ライナー摺動面より離れる“浮き上がり”を評価するため、万能試験機を用いて、ライナーと骨頭との摺動面に生じる吸着力を検討した。

蒸留水環境下において、CLPE の吸着力は、離れ速度に関わらず低い値を示した。これに対し、PMPC 処理 CLPE ライナーのそれは、離れ速度が 5 mm/min から 100 mm/min に増加するにともなって増加したが、その後、200 mm/min 以上の離れ速度では徐々に低下した。蒸留水環境下において、50～100 mm/min の速度で骨頭を引き抜いたとき、PMPC 処理 CLPE ライナーと骨頭の吸着力は、CLPE ライナーと骨頭のそれに比べ 2.6～8.8 倍と高い値を示した。これらの増加は、MPC 層が保持した水による表面張力、MPC 層の粘性抵抗などが影響したと考えられる。

ウシ血清環境下では、離れ速度が 5～200 mm/min の範囲において、CLPE および MPC 処理 CLPE ライナーの吸着力は低い値でほぼ一定であった。その後、MPC 処理 CLPE の吸着力は離れ速度が 500 mm/min に増加しても変化なかったのに対し、CLPE ライナーのそれは増加した。CLPE ライナーと骨頭の界面では、各々の表面に吸着した血清由来のタンパク質が粘性抵抗となり吸着力を高めたと考えられる。これに対し、MPC 処理 CLPE 表面ではタンパク質の吸着が抑制される一方、Co-Cr 表面にはタンパク質が吸着する。つまり、MPC 層とタンパク質との間に吸着力が発生し難い上に、MPC 処理 CLPE 表面と Co-Cr 骨頭表面の直接接触が防がれる効果が与えられるため、低い値で一定となったと考えられる。

ヒアルロン酸製剤環境下で得られた吸着力はいずれも、水およびウシ血清環境下で得られたそれらに比べ、高い値を示した。これは、水、ウシ血清に比べ、ヒアルロン酸製剤の粘度が高いことに由来すると考えられる。

E. 結論

今年度は、大腿骨コンポーネントの頚部が寛骨臼コンポーネントの周縁部に接触するまでの関節可動域を指標として、（1）骨董径が与える影響を算出した。続いて、下肢の自重によって骨頭が引き下げられライナー面から離れる「浮き上がり防止」については、ライナー摺動面—骨頭間の吸着力を指標として、ライナー面の Poly（MPC）（PMPC）処理が与える影響—を検討した。関節摺動面の安定性のための関節可動域の増大には、関節面を構成する骨頭部分の大径化が有効であることが確認された。また、関

節摺動面の吸着性を向上するために、MPC ポリマーを用いた処理は有効である可能性が示唆された。次年度以降はこのモデルを用いて関節摺動面の安定性・吸着性を向上する新しいインプラントの形状検討する予定である。

F. 健康危険情報

特になし。

G. 研究発表

1. 論文発表

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別紙4

研究成果の刊行に関する一覧表レイアウト

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Superlubricious surface mimicking articular cartilage by grafting poly(2-methacryloyloxyethyl phosphorylcholine) on orthopaedic metal bearings

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Abstract: Aseptic loosening of the artificial hip joint with osteolysis due to the wear particles from polyethylene cup has remained as a serious issue. To reduce this wear and develop a novel artificial hip joint system, we produced a superlubricious metal-bearing material: for this, we grafted a 2-methacryloyloxyethyl phosphorylcholine (MPC) polymer onto the surface of a cobalt–chromium–molybdenum (Co-Cr-Mo) alloy. For ensuring long-term benefit retention of poly(MPC) on the Co-Cr-Mo alloy for application as a novel artificial hip joint system, several issues must be considered: strong bonding between poly(MPC) and Co-Cr-Mo surface, high mobility of free end groups of the poly(MPC) layer, and high density of the introduced poly(MPC). Considering these issues, we introduced a 3-methacryloxypropyl trimethoxysilane (MPSi) intermediate layer and a photoinduced graft polymerization technique to create a strong covalent bond between the Co-Cr-Mo substrate and the poly(MPC) chain via the MPSi layer. The thickness and density of the poly(MPC) layer on the surface increased with the MPC concentration and photoirradiation time. The grafted poly(MPC) layer successfully provided super-lubricity to the Co-Cr-Mo surface. The poly(MPC)-grafted crosslinked polyethylene/poly(MPC)-grafted Co-Cr-Mo or cartilage/poly(MPC)-grafted Co-Cr-Mo bearing interface mimicking natural joints showed an extremely low friction coefficient of 0.01, which is as low as that of natural cartilage interface. A superlubricious metal-bearing surface would enable the development of a novel biocompatible artificial hip joint system-artificial femoral head for partial hemiarthroplasty and metal-on-polymer/metal type for total hip arthroplasty. © 2008 Wiley Periodicals, Inc. J Biomed Mater Res 91A: 730–741, 2009

Key words: joint replacement; metal surface treatment; photopolymerization; phosphorylcholine; hydrophilicity

INTRODUCTION

Every year, the number and prevalence of primary and revision hip and knee joint replacements increases substantially worldwide.[1] As a result, the quality of artificial joints is becoming increasingly important. Most patients who receive an artificial joint experience dramatic pain relief and rapid improvement in both their daily activities and quality of life. The most widely used bearing couple in artificial hip joint systems is a combination of an ultrahigh molecular weight polyethylene (UHMWPE) acetabular component and a metal femoral component. Cobalt–chromium–molybdenum (Co-Cr-Mo) alloy is one of the most widely used metal bearing materials in artificial joint systems. The Co-Cr-Mo alloy has good mechanical properties, castability, corrosion resistance, and wear resistance, whereas stainless steel and titanium alloys have a disadvantage with regard to corrosion resistance and wear resistance, respectively.

In total hip arthroplasty (THA), osteolysis caused by the wear particles from UHMWPE has been recognized as a serious issue.[2–4] Efforts to decrease

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these particles have focused on bearing material improvement and the use of combinations other than metal-on-UHMWPE.[5–7] Recently, a metal-on-metal type artificial hip joint system consisting of Co-Cr-Mo acetabular and femoral components has been studied.[8] The advantages of the Co-Cr-Mo/Co-Cr-Mo bearings are that they do not generate UHMWPE wear debris and they exhibit decreased wear when compared with Co-Cr-Mo/UHMWPE bearings.[9,10] However, even in Co-Cr-Mo/Co-Cr-Mo bearings, aseptic loosening induced by wear particles and metallosis remains as serious issue in revision surgeries.[11,12] In addition to metallosis, electrochemical corrosion and carcinogenesis occurring due to the dissemination of wear particles to the other parts of the body have been reported.[13]

On the other hand, improvements in the bearing materials and surface modifications of the Co-Cr-Mo alloy have been attempted, in order to reduce such wear particles.[14,15] Surface coating may reduce the wear without compromising the bulk mechanical properties of the implant materials. Various "hardening treatments" of metal bearing surfaces, such as diamond-like carbon coating, titanium nitride coating, and ion implantation have also been attempted.[16,17] Although these surface modifications may improve THA survivorship, the limited THA longevity imposes restrictions for its application to younger patients. Consequently, the possibility of replacing the femoral head alone, whether solid or articular surface replacement, remains an attractive feature of such implants during revision surgeries of THA. However, the Co-Cr-Mo alloy or the hardening-treated Co-Cr-Mo alloy may induce damage to cartilaginous tissue.

In contrast, the previous study reported that highly lubricious hydrogel polymer used as an artificial cartilage did not damage cartilaginous tissue.[18] We have recently developed a highly lubricious artificial hip joint system by a "mild treatment" with soft materials. In this treatment, poly(2-methacryloyloxyethyl phosphorylcholine) (MPC) was grafted onto the surface of CLPE (CLPE-*g*-MPC).[19–21] MPC is a methacrylate with a phospholipid polar group in a side chain, and it has both good solubility in polar solvents including water and polymerization ability by conventional radical polymerization.[22] Many MPC polymers have been widely investigated as biomaterials.[23–27] As a result, various medical devices have already been developed using MPC polymers, and they are being used clinically. The efficacy of MPC polymers as biomaterials has been well verified.[28–30]

In general, there are two methods for modifying the polymer surface. The first method involves surface absorption or reaction with small molecules,[31,32] and the second is grafting polymeric molecules onto the substrate through covalent bonding.[33] Most frequently, grafting polymerization is performed using either of the following methods: (1) surface-initiated graft polymerization, termed as the "grafting from" method, in which monomers are polymerized from initiators or comonomers and (2) adsorption of the polymer to the substrate, termed as the "grafting to" method (i.e., dipping, crosslinking, and ready-made polymers with reactive end groups reacting with the functional groups of the substrate).[34,35] In our previous study, the Co-Cr-Mo-*g*-MPC prepared by the adsorption of the polymer to the Co-Cr-Mo substrate, termed as the "grafting to" method, was not uniform, and the CLPE-*g*-MPC/Co-Cr-Mo-*g*-MPC bearing couples showed high friction.[36] These results were probably ascribed to a low density of the poly (MPC) on Co-Cr-Mo prepared by the "grafting to" method. To solve the issue in this study, we developed a superlubricious surface with nanometer-scale poly(MPC) modification and was accomplished by using a photo-induced radical polymerization technique that was similar to the one used in the "grafting from" method. The "grafting from" method has an advantage over the "grafting to" method in that it synthesizes a high-density polymer brush.

To ensure *in vivo* long-term retention of this poly(MPC) graft on the Co-Cr-Mo alloy, it is necessary to create strong covalent bonding between the Co-Cr-Mo alloy substrate and the poly(MPC) graft chain. Organosilanes have already been known as surface coupling agents to enhance bonding between a metal or a metal oxide surface and an organic resin such as dental resin, and they can strongly bind metals to resins in dental implants.[37] Organic silanes or silane coupling agents comprise at least a hydrolyzable alkoxysilyl or chlorosilyl group and an organofunctional group.[38] The agents are effective to introduce organofunctional groups into the siloxane network polymer. The organofunctional group in the silane could be useful to improve bonding with the organic overlayer. 3-Methacryloxypropyl trimethoxysilane (MPSi) is a simple surface coupling agent consisting of three methoxysilane groups, a propyl chain, and a functional methacrylate, and the structure of its main chain is equivalent to that of MPC.

In this study, based on the hypothesis that the "grafting from" method has advantages over the "grafting to" method in that it can synthesize a uniformly and controllable polymer layer, a superlubricious metal bearing material in which the poly(MPC) with biocompatibility and hydrophilicity was grafted onto the surface of the Co-Cr-Mo alloy (Co-Cr-Mo-*g*-MPC) has been introduced for developing a novel artificial hip joint system, that is, artificial femoral head and metal-on-metal (Co-Cr-Mo/Co-Cr-Mo) type for THA. The surface structure and preliminary tribological properties of Co-Cr-Mo-*g*-MPC were also investigated.

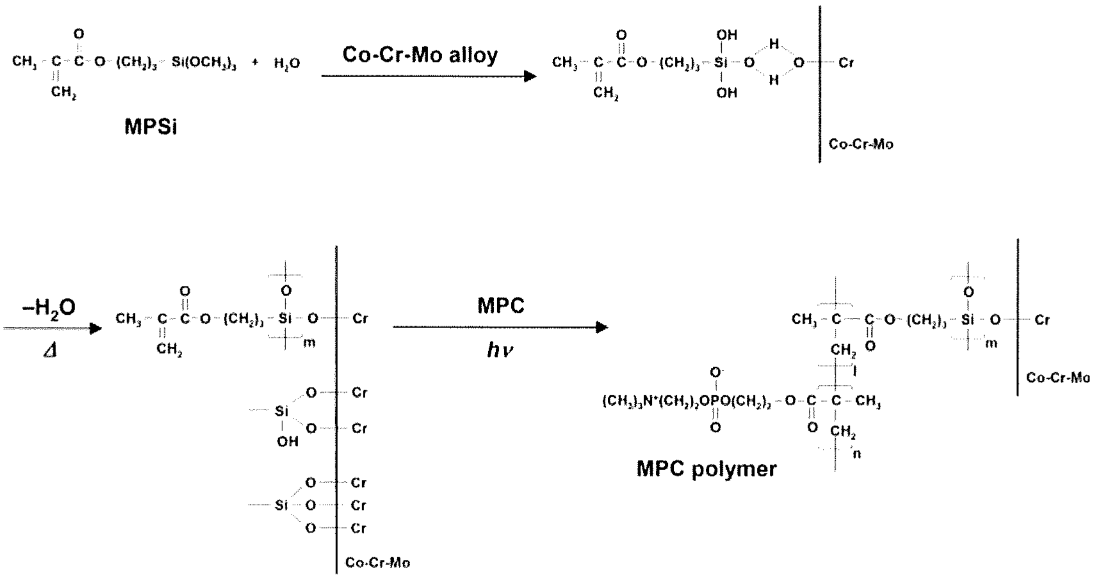

Figure 1. Chemical reaction on Co-Cr-Mo during polymerization of MPC.

MATERIALS AND METHODS

Chemicals

MPC was synthesized industrially by using the method developed by Ishihara et al.,[22] and it was supplied by NOF Corp. (Tokyo, Japan). MPSi was purchased from Shin-Etsu Chemical Co., Ltd. (Tokyo, Japan). Succinic acid and ethanol were purchased from Kanto Chemical Co., Inc. (Tokyo, Japan). 2-Hydroxy-l-[4-(hydroxyethoxy)phenyl]-2-methyl-lpropanone (DAROCUR® 2959; D2959) was purchased from Ciba Specialty Chemicals Holding Inc. (Basel, Switzerland). D2959 is a highly efficient radical photoinitiator for ultraviolet (UV) curing of the systems containing unsaturated monomers and prepolymers, and it is particularly well known as a cytocompatible UV photoinitiator with UV intensities of <6 mW/cm^2 that can perform polymerization for up to 10 min with a UV light of 365 nm.[39]

Co-Cr-Mo alloy substrate and pretreatments

The Co-Cr-Mo alloy was supplied by Yoneda Advanced Casting Co., Ltd (Takaoka, Japan). This alloy was manufactured according to the ASTM F75 standard specification for Co-28Cr-6Mo alloy.[40] The Co-Cr-Mo samples were polished so that the average surface roughness ranged between 0.01 and 0.02 μm.

The polished Co-Cr-Mo samples were washed with acetone and then immersed in 35 vol % nitric acid at room temperature for 35 min according to the ASTM F86-04 standard.[36,41] This treatment results in passivation by surface oxidation, and it could lead to the dissolution of certain foreign materials that may remain from the previous procedure. Moreover, a previous study reported that the surface of as-polished Co-Cr-Mo alloy might lack the Cr content that the bulk possesses, and that surface etching by nitric acid treatment would have produced a Cr-rich surface layer.[36] We therefore treated the surface with nitric acid with the aim of increasing the Cr concentration by "resurfacing."

After the nitric acid treatment, the Co-Cr-Mo samples were irradiated with O_2 plasma at a 500-W high-frequency output and 150-mL/min O_2 gas flow for 5 min by using an O_2 plasma etcher (PR500, Yamato Scientific Co., Ltd., Tokyo, Japan). The O_2 plasma treatment increased the thickness of the surface oxide layer.[42]

MPSi silanization and MPC graft polymerization

The synthesis of Co-Cr-Mo-*g*-MPC is schematically illustrated in Figure 1. The pretreated Co-Cr-Mo samples were immersed in an ethanol solution containing 5 mass % MPSi, 1 mass % succinic acid, and 0.1 mass % D2959 at room temperature for 12 h for silanization of the trimethoxysilane group. In this study, D2959 was used as a photoinitiator for surface-initiated polymerization so as to be included in the MPSi layer. Generally, for surface-initiated polymerization, such an initiator covalently bonded to the substrate to yield a "grafting from" polymerization is usually used. They were then annealed at 70°C for 3 h in air for dehydration. The MPC was dissolved in degassed pure water to attain concentrations ranging from 0.25 to 1.00 mol/L. Subsequently, the MPSi (containing D2959)-coated Co-Cr-Mo samples were immersed in aqueous MPC solutions. Photoinduced graft polymerization on the Co-Cr-Mo surface was performed using ultraviolet irradiation (UVL-400HA ultra-high pressure mercury lamp; Riko-Kagaku Sangyo Co., Ltd., Funabashi, Japan) with an intensity of 5 mW/cm^2 at 60°C for 23–180 min; a filter (Model D-35; Toshiba Corp., Tokyo, Japan) was used restrict the passage of ultraviolet light to wavelengths of 350 ± 50 nm. After the polymerization, the Co-Cr-Mo-*g*-MPC samples were removed from the solution, washed with pure water and ethanol, and dried at room temperature. For purification, washing with pure water and ethanol enables the removal of the free poly(MPC) and/or poly(MPC-*co*-MPSi) adsorbed on the Co-Cr-Mo surface.[43]

MPC graft polymerization on crosslinked polyethylene

Compression-molded UHMWPE (GUR1020 resin, Poly Hi Solidur Inc., IN) bar stock was gamma-ray irradiated at 50 kGy in N_2 gas and annealed at 120°C in N_2 gas for crosslinking. After cooling, the crosslinked polyethylene (CLPE) specimens were machined from this bar stock.

MPC grafting onto the CLPE surface was performed as described in previous studies.[43–45] The CLPE specimens were immersed in an acetone solution containing 10 mg/mL benzophenone for 30 s and then dried in the dark at room temperature to remove the acetone. MPC was dissolved in degassed pure water to a concentration of 0.5 mol/L. The benzophenone-coated CLPE samples were immersed in the aqueous MPC solution. Photoinduced graft polymerization on the CLPE surface was carried out using UV irradiation with an intensity of 5 mW/cm^2 at 60°C for 90 min. After the polymerization, the CLPE-*g*-MPC samples were removed from the solution, washed with pure water and ethanol, and dried.

Articular cartilage from porcine ankle joint

Using a surgical hand corer or surgical saw, articular cartilage specimens were harvested from the flat part of the ankle joint of the fresh frozen porcine tibia (ages 6–9 months) for friction test. Pin-type articular cartilage specimens were shaped as cylinders with a height of 5 mm and diameter of 9 mm, and they had ~1 mm of cartilage layer and subcondral bone used for mounting. Throughout the procedure, the articular cartilage surface was hydrated regularly with Dulbecco's phosphate-buffered saline (PBS, pH 7.4, ion strength = 0.15 M; Immuno-Biological Laboratories Co., Ltd., Takasaki, Japan). All the articular cartilage specimens were then stored in Dulbecco's PBS and frozen at −80°C.[46]

Surface analysis by Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, and water-contact angle measurement

The functional group vibrations of the Co-Cr-Mo alloy surfaces before and after the MPC grafting were examined by Fourier-transform infrared (FTIR) spectroscopy with attenuated total reflection (ATR) equipment. The FTIR/ATR spectra were obtained using an FTIR analyzer (FT/IR615, JASCO Co. Ltd., Tokyo, Japan) for 32 scans (1.2 s/scan) over the range of 800–2000 cm^{-1} at a resolution of 4.0 cm^{-1}.

The surface elemental conditions of the Co-Cr-Mo alloy before and after the MPC grafting were analyzed by X-ray photoelectron spectroscopy (XPS). The XPS spectra were obtained using an XPS spectrophotometer (AXIS-HSi165, Kratos/Shimadzu Corp., Kyoto, Japan) equipped with a 15-kV MgKα radiation source at the anode. The take-off angle of the photoelectrons was maintained at 90°. Five scans (~260 to 425 s/scan depending on the atomic signal strength) were taken for each sample.

The static-water contact angles on the Co-Cr-Mo surfaces that were subjected to different types of pretreatments before and after the MPC grafting were measured by the sessile drop method using an optical bench-type contact angle goniometer (Model DM300, Kyowa Interface Science Co., Ltd., Saitama, Japan). Drops of purified water (1 μL) were deposited on the Co-Cr-Mo-*g*-MPC surface, and the contact angles were directly measured with a microscope after 60 s of dropping, according to the ISO 15989 standard.[47] Measurements were repeated six times for each sample, and the average values were considered as the contact angles.

Cross-sectional observation by transmission electron microscopy

A crosssection of the poly(MPC) layer on the Co-Cr-Mo surface was observed using a transmission electron microscope (TEM) and by energy dispersive X-ray (EDX) spectroscopy. The specimens were precoated with an aluminum film using a focused ion beam (FIB) system to prevent charging. After precoating, a thin film of the samples was prepared by the FIB technique using an FB-2000A (Hitachi High-Technologies Co., Tokyo, Japan) FIB system. The samples were thinned to electron transparency by a low gallium ion beam current. The thin film thus prepared was positioned onto a copper TEM mesh grid. TEM observations were then recorded using an HF-2000 electron microscope (Hitachi High-Technologies Co.) at an acceleration voltage of 200 kV. EDX spectra were analyzed on a crosssection of the untreated Co-Cr-Mo sample and the Co-Cr-Mo-*g*-MPC sample obtained with 0.50 mol/L MPC concentrations and a 90-min photoirradiation time using a Sigma EDX attachment (Kevex Instruments, Inc., Valencia, CA) at an acceleration voltage of 200 kV. The probe size of the electron beam was maintained at 1 nm.

Friction test

The coefficients of dynamic friction between the pins fabricated from various materials (Co-Cr-Mo, CLPE, CLPE-*g*-MPC, and articular cartilage) and the untreated Co-Cr-Mo or Co-Cr-Mo-*g*-MPC (obtained with 0.50 mol/L MPC concentrations and a 90-min photoirradiation time) plates were measured using a pin-on-plate machine (Tribostation 32; Shinto Scientific Co., Ltd., Tokyo, Japan) as the preliminary test for tribological properties. Each pin was a cylinder measuring 5 mm in height and 9 mm in diameter and used to prepare five sample pieces. The friction tests were performed at room temperature with a load of 0.98 N, sliding distance of 25 mm, and frequency of 1 Hz for a maximum of 100 cycles.[48] Pure water was used as a lubricant. The mean coefficients of dynamic friction were determined by averaging five data points from the 100 (96–100) cycle measurements. Standard analysis of variance (ANOVA) was applied to the data of the (at 100 cycles) existed among the eight groups (Co-Cr-Mo, CLPE, CLPE-*g*-MPC, Cartilage pins against untreated Co-Cr-Mo and Co-Cr-Mo-

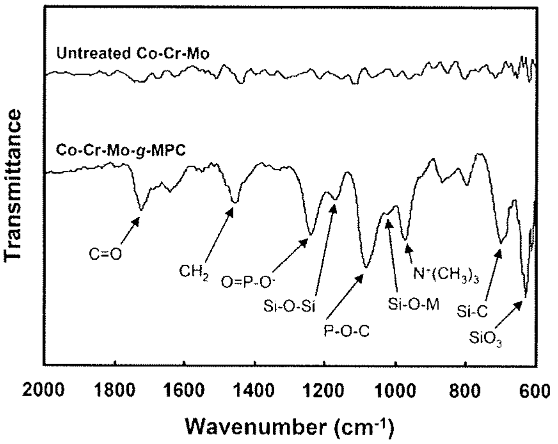

Figure 2. FTIR/ATR spectra of untreated Co-Cr-Mo and Co-Cr-Mo-*g*-MPC surfaces with a 0.50-mol/L MPC concentration and a 90-min photoirradiation time.

g-MPC plates, respectively), in this study. Two combinations (e.g., Co-Cr-Mo pin against untreated Co-Cr-Mo and Co-Cr-Mo-*g*-MPC plates, Co-Cr-Mo and CLPE pins against Co-Cr-Mo-*g*-MPC plate) were especially made with the Student's *t* test ($p < 0.05$).

RESULTS

Figure 2 shows the FTIR/ATR spectra of the Co-Cr-Mo sample and that of photoirradiated grafting of MPC under 0.50-mol/L MPC concentration and 90-min photoirradiation time. Absorption peaks were not observed for the Co-Cr-Mo sample before the MPC graft polymerization in the wavenumber range of 800–2000 cm^{-1}. In contrast, absorption peaks were newly observed only for the Co-Cr-Mo-*g*-MPC samples. The peaks at 1720, 1550, and 1460 cm^{-1} are attributed to C=O and —CH$_2$— in the MPSi and poly(MPC) graft chains. The peaks at 1180, 1040, 700, and 630 cm^{-1} are attributed to the trimethoxysilane group in the MPSi unit.[49] The peaks at 1240, 1080, and 970 cm^{-1} are attributed to the —N$^+$(CH$_3$)$_3$ and phosphate groups in the MPC unit.[44]

In the XPS spectra of the binding energy region of the nitrogen (N$_{1s}$), phosphorous (P$_{2p}$), and silicon (Si$_{2p}$) electrons, peaks appeared in the case of Co-Cr-Mo-*g*-MPC; however, they were not observed in the case of Co-Cr-Mo (Fig. 3). The peak at 104 eV was attributed to the Si$_2$O$_3$ or SiO$_2$ in the trimethoxysilane group in the MPSi unit. The peaks at 403 and 134 eV were attributed to the —N$^+$(CH$_3$)$_3$ and phosphate groups, respectively. These peaks reflect the phosphorylcholine present in the MPC units. Figure 4 shows the Si, N, and P concentrations of the Co-Cr-Mo-*g*-MPC surface as a function of the photoirradiation time during polymerization for various MPC concentrations in feeds. Both the N and P concentrations in the Co-Cr-Mo-*g*-MPC surface increased with the photoirradiation time. In the case of higher MPC concentrations, when the photoirradiation time was greater than 90 min, the N and P concentrations became almost constant above 5.0 atom%. These values were almost equivalent to the theoretical elemental composition (N = 5.3 atom%, P = 5.3 atom%) of poly(MPC). As a trade off, the Si concentration at the Co-Cr-Mo-*g*-MPC surface decreased with an increase in the photoirradiation time.

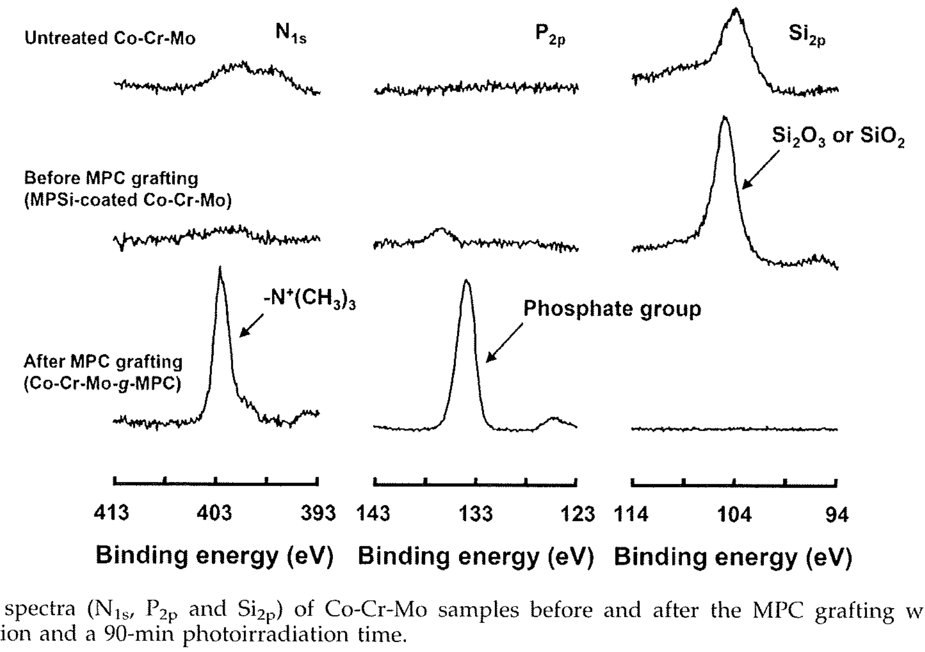

Figure 3. XPS spectra (N$_{1s}$, P$_{2p}$ and Si$_{2p}$) of Co-Cr-Mo samples before and after the MPC grafting with a 0.50-mol/L MPC concentration and a 90-min photoirradiation time.

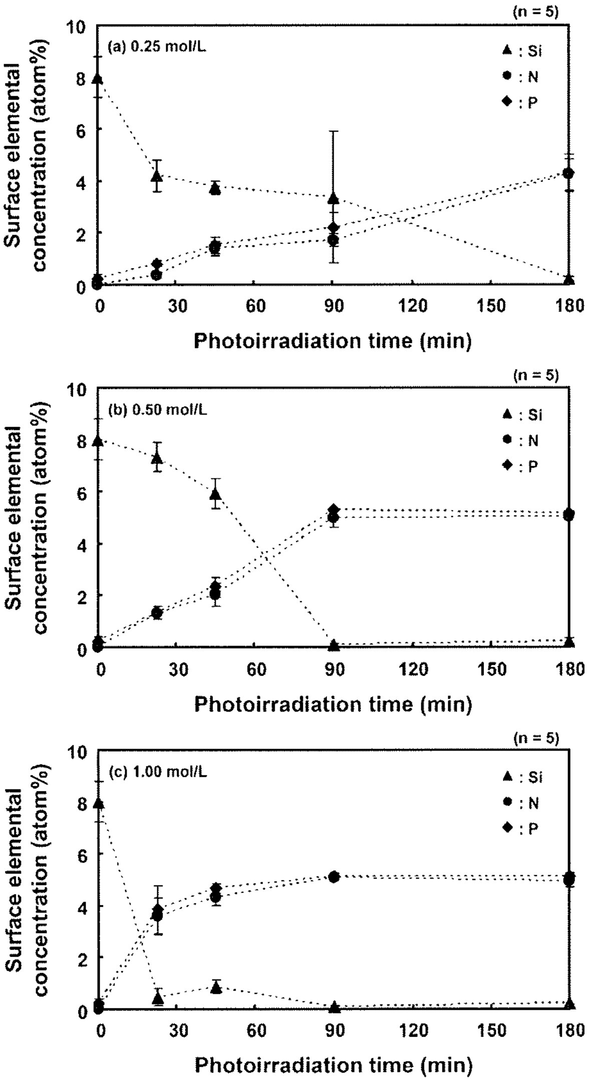

Figure 4. Surface elemental concentrations in the Co-Cr-Mo-*g*-MPC surface as a function of the photoirradiation time for various MPC concentrations in feeds. Bar: standard deviations.

Figure 5 shows the static-water contact angle on the Co-Cr-Mo-*g*-MPC surface as a function of the photoirradiation time during polymerization with various MPC concentrations in feeds. The static-water contact angle on the untreated Co-Cr-Mo surface before the MPC grafting was ~80°. The static-water contact angle on the Co-Cr-Mo-*g*-MPC surface decreased markedly with an increase in the photoirradiation time and the MPC concentration. When the photoirradiation time and MPC concentration were greater than 90 min and 0.50 mol/L, respectively, the static-water contact angle became constant at a low value of 20°.

Figure 6 shows the cross-sectional TEM images of Co-Cr-Mo-*g*-MPC obtained with various MPC concentrations and a 90-min photoirradiation time. In the Co-Cr-Mo-*g*-MPC, a 10 to 360-nm thick poly(MPC) layer was clearly observed on the surface of the Co-Cr-Mo substrate. The thickness of the poly(MPC) layer increased with the MPC concentration during polymerization. At an MPC concentration of 1.00 mol/L, the thickness of the poly(MPC) layer was greatest, that is, 360 nm. These results indicate that the length of the poly(MPC) chain (thickness of the poly(MPC) layer) can be controlled by adjusting the MPC concentration during polymerization. This is explained by the fact that the length of the polymer chains produced in a radical polymerization reaction generally correlates with the MPC concentration.

Figure 7 shows the EDX spectra of the untreated Co-Cr-Mo and Co-Cr-Mo-*g*-MPC obtained with a 0.5-mol/L MPC concentration and a 90-min photoirradiation time. In spectra (P1) and (P3) of the substrate of the untreated Co-Cr-Mo and Co-Cr-Mo-*g*-MPC, strong peaks were observed at 0.8, 2.3, 5.4, 6.0, 6.9, and 7.7 keV. These peaks are attributed to the Co, Cr, and Mo atoms in the Co-Cr-Mo substrate. In spectrum (P2) of the surface of the untreated Co-Cr-Mo, a peak was observed at 0.5 keV. This peak is attributed to the O atom in the metal oxide layer of the Co-Cr-Mo. In spectrum (P4) of the intermediate layer of the Co-Cr-Mo-*g*-MPC, peaks were observed at 0.5 and 1.7 keV. These peaks are attributed to the O and Si atoms in the intermediate layer between the silane of the MPSi and the metal oxide of the Co-Cr-Mo. In spectra (P4) and (P5) of the intermediate layer and the poly(MPC) layer of the Co-Cr-Mo-*g*-MPC, a significant peak attributed to the P atom was observed at 2.0 keV. This peak is mainly attributed to the MPC units. Several spectra exhibited

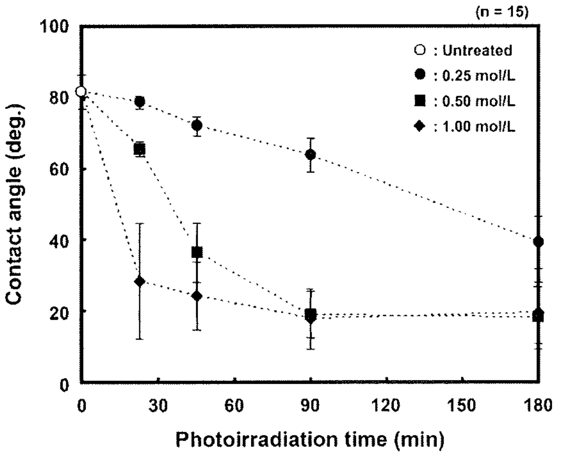

Figure 5. Static-water contact angle of the Co-Cr-Mo-*g*-MPC surface as a function of the photoirradiation time for various MPC concentrations in feeds. Bar: standard deviations.

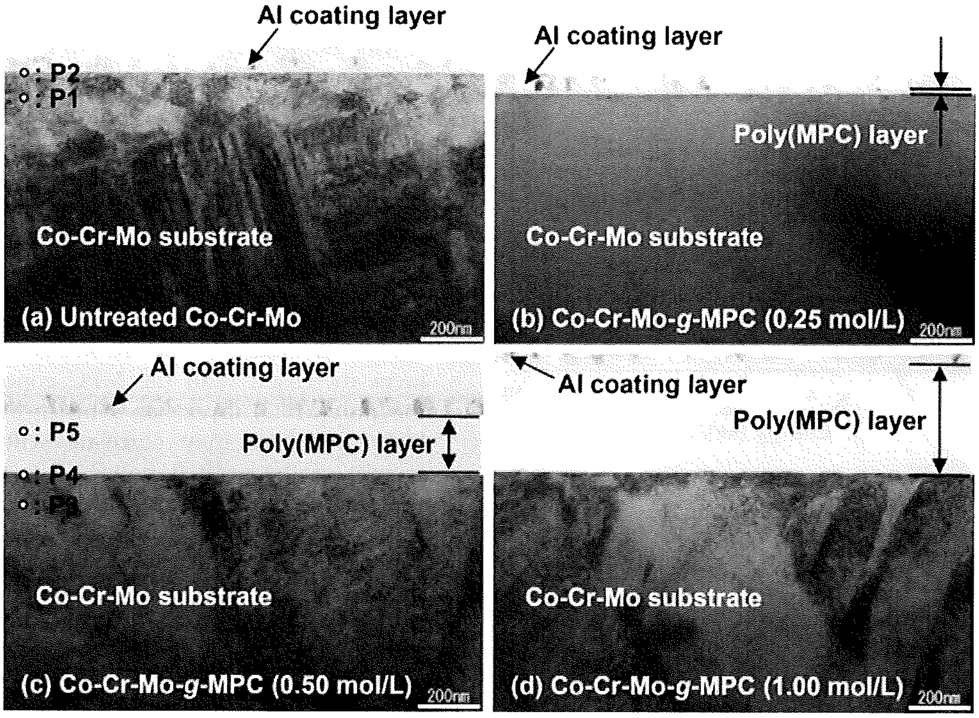

Figure 6. Cross-sectional TEM images of the Co-Cr-Mo-*g*-MPC surface with various MPC concentration in feeds and a 90-min photoirradiation time. Aluminun coating layers (~70 nm) for preparation of TEM observation specimen are shown above the poly(MPC) layer of the Co-Cr-Mo-*g*-MPC surface. In (a) and (c), small open-circles (P1-5) indicate EDX analysis points. Bar: 200 nm.

peaks at 1.5, 8.0, and 8.9 keV. In these cases, the peaks are attributed to the Al and Cu atoms of the Aluminum coating for the preparation of the TEM observation specimen and/or the copper TEM mesh grid.

Figure 8 shows the coefficients of dynamic friction of the sliding couples, namely, untreated Co-Cr-Mo, CLPE, CLPE-*g*-MPC, and articular cartilage pins sliding against the untreated Co-Cr-Mo and Co-Cr-Mo-*g*-MPC plates. The Co-Cr-Mo/Co-Cr-Mo and CLPE/Co-Cr-Mo couples showed a high friction coefficient of ~0.19 and 0.14 in the initial 10 cycles; especially, the value of the Co-Cr-Mo/Co-Cr-Mo couple increased and reached ~0.41 in the 100 cycles ($p < 0.005$). After the friction test, some scratches parallel to the sliding direction were clearly observed in the Co-Cr-Mo/Co-Cr-Mo bearing area. The CLPE-*g*-MPC/Co-Cr-Mo couples showed a low friction coefficient of about 0.05 for both 10 and 100 cycles. This corresponds to ~70% reduction ($p < 0.001$ in both cycles) when compared with the coefficients of untreated CLPE/Co-Cr-Mo couples. The coefficients of dynamic friction of all types of pins sliding against the Co-Cr-Mo-*g*-MPC couples decreased drastically when compared with those of untreated Co-Cr-Mo couples. The degree of reduction in the coefficient was ~90% (80–99%) for both 10 and 100 cycles ($p < 0.001$ in all types of pins). In particular, in the CLPE-*g*-MPC/Co-Cr-Mo-*g*-MPC couple, the poly(MPC) layer sliding against the poly(MPC) layer showed the lowest friction coefficient of ~0.005, and this value was almost steady during the experiment. The friction coefficient of the cartilage/Co-Cr-Mo couple increased gradually and reached ~0.09 in the 100 cycles. The friction coefficient of the cartilage/Co-Cr-Mo-*g*-MPC couple was ~0.006 in the 100 cycles, and it remained almost steady. This was much lower than the friction coefficient of the cartilage/Co-Cr-Mo couple ($p < 0.001$).

DISCUSSION

In this study, based on the hypothesis that the "grafting from" method has advantages over the "grafting to" method in that it synthesizes a uniformly and controllable polymer layer, a superlubricious Co-Cr-Mo alloy surface by poly(MPC) grafting was prepared for its application to artificial joints with the aim of reducing wear. Several important issues are involved in the long-term retention of the benefits of poly(MPC) used in artificial joints under variable and multidirectional loads: strong bonding

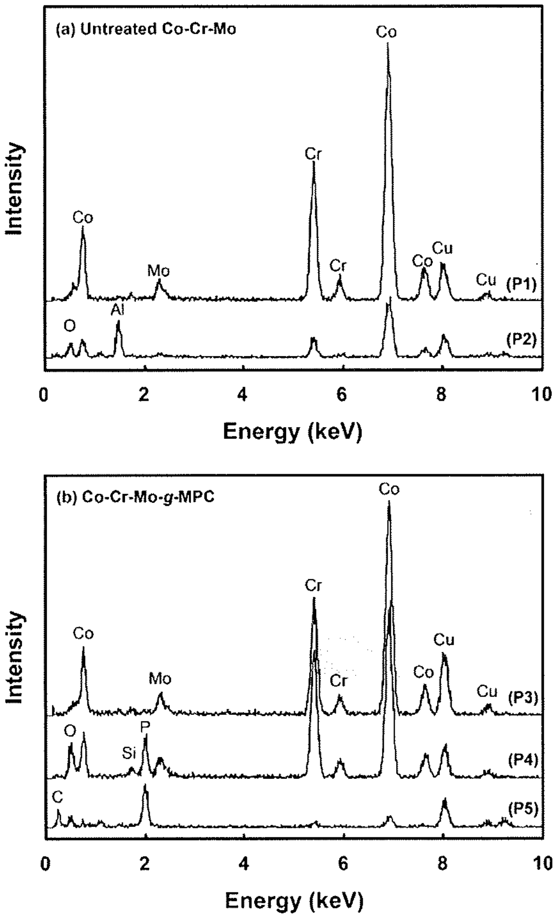

Figure 7. EDX spectra of the Co-Cr-Mo-*g*-MPC surface with a 0.5-mol/L MPC concentration and a 90-min photoirradiation time. The spectra were analyzed on the cross-section (P1–5) of the untreated Co-Cr-Mo and Co-Cr-Mo-*g*-MPC in Figure 6.

between the poly(MPC) and the Co-Cr-Mo surface, high mobility of the free end groups of the poly (MPC) layer, and a high density of the introduced poly(MPC). Taking these issues into consideration, the photoinduced radical graft polymerization technique and the MPSi intermediate layer were used to obtain covalent bonding between the Co-Cr-Mo substrate and the poly(MPC) chain via the MPSi layer.

Figure 4 shows the N and P concentrations of the Co-Cr-Mo-*g*-MPC surface obtained with a 0.5-mol/L MPC concentration and a 90-min photoirradiation time; the concentrations became almost constant at high values of 5.0 and 5.3 atom%, respectively. These values were almost equivalent to the theoretical elemental composition of poly(MPC). In addition, the static-water contact angle of the Co-Cr-Mo-*g*-MPC surface became constant at a low value of 20°, showing a highly hydrophilic nature. The peak attributed to Si atoms was observed in the intermediate layer between the poly(MPC) layer and Co-Cr-Mo substrate only, as shown in Figure 7. Therefore, it was thought that the poly(MPC) chain was grafted and that it extended from the methacrylate on the MPSi. The hydrophilic layer was formed with the poly(MPC) chain, which attained high mobility, and the poly(MPSi) chain existed as the immobilized end-group of the poly(MPC) graft chains.

In Figure 4, both the N and P concentrations in the Co-Cr-Mo-*g*-MPC surface attributed to poly (MPC) increased with the MPC concentration during polymerization. In addition, in the TEM images shown in Figure 6, the thickness of the poly(MPC) layer increased with the MPC concentration. When the poly(MPC) layer has a brush-like structure, the layer thickness may correlate with the molecular weight of the grafted poly(MPC). The high-density poly(MPC) graft chains in the Co-Cr-Mo-*g*-MPC are assumed to exhibit a brush-like structure.[24,50] It is generally well known that the reaction rate of radical polymerization is extremely high.[51] In this study, the length (molecular weight) of the poly(MPC) graft chains was successfully controlled by the MPC concentration used for polymerization as a feed solution. This indicates that the length of the poly(MPC) chain grafted on the Co-Cr-Mo surface increased with the MPC concentration in feed.[45]

The previous study by the authors reported that the density of the poly(MPC) chains on the surface of the CLPE prepared by photoinduced radical polymerization gradually increased with the irradiation

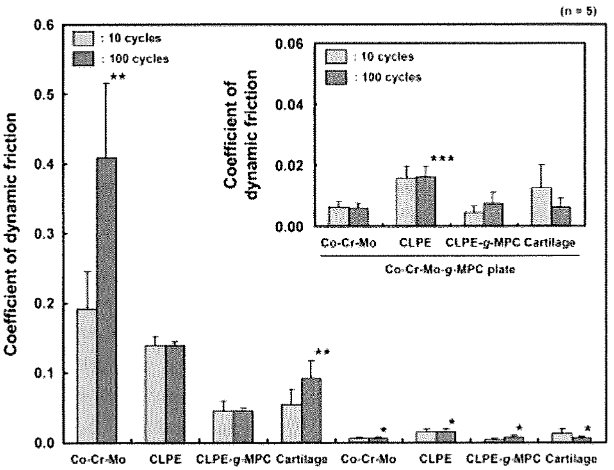

Figure 8. Coefficients of dynamic friction for the various types of pins sliding against the untreated Co-Cr-Mo and Co-Cr-Mo-*g*-MPC plates. Bar: standard deviations. **t* test, significant difference ($p < 0.001$) when compared with the untreated Co-Cr-Mo plate, ***t* test, significant difference ($p < 0.001$) when compared with the coefficients of dynamic friction at 10 cycles, and ****t* test, significant difference ($p < 0.001$) when compared with the Co-Cr-Mo pin against Co-Cr-Mo-*g*-MPC plate.

time. The study also showed that the entire surface of the CLPE was coated using polymerization times longer than 45 min with almost the same thickness as that of the poly(MPC) layer for longer irradiation times (100–200 nm).[44] In this study, both the N and P concentrations in the Co-Cr-Mo-*g*-MPC surface attributed to poly(MPC) increased with the photoirradiation time. When the MPC concentration was greater than 0.5 mol/L, the N and P concentrations of the Co-Cr-Mo-*g*-MPC surface increased to $\sim$5.3 atom%, which was almost equivalent to the theoretical elemental composition of poly(MPC). In addition, the Co-Cr-Mo-*g*-MPC surface obtained with a 0.5-mol/L MPC concentration and a 90-min photoirradiation time retained the uniform poly(MPC) layer with a thickness of 200 nm, as reported in the previous study. These observations indicate that irradiation time control is essential to obtain a high-density poly(MPC) layer.[44]

Several previous studies reported that a silane coating has a low water resistance due to hydrolysis of siloxane bond and to desorption of physisorbed silane. Zhang et al.[52] and others[53,54] reported that the limited stability of the Si—O—metal (M) bond against hydrolysis is the main reason for the limited stability in water, and the water stability could be improved by using several factors: (1) an induction of bridged silane coupling agents, when hydrolyzed, contain two or more $-Si(OH)_3$, (2) the hydrophobic alkyl moieties which limit the contact with water, and (3) a increase of thickness of surface oxide layer. Therefore, we used the MPSi intermediate layer with three methoxysilane groups and a functional methacrylate and the pretreatment (nitric acid treatment and O_2 plasma treatment) for Co-Cr-Mo surface were used.

MPSi binds to the Co-Cr-Mo substrate by a condensation reaction in two steps (Fig. 1). In the first step, the MPSi is hydrolyzed (activated), and in the second step, the hydrolyzed silane molecule binds to the surface by an Si-O—M bond, forming branched hydrophobic siloxane bonds, Si-O-Si.[38,49] The hydrolyzed silane molecule has three —OH groups that can react with the —OH groups of the surface metallic oxide layer to form siloxane bonds covalently. The peaks at 1180 and 1040 cm^{-1} in the FTIR/ATR spectrum of the Co-Cr-Mo-*g*-MPC surface were attributed to Si—O—Si and Si—O—M, respectively (Fig. 2), and these were observed after the MPC grafting. This suggests that the trimethoxysilane group of MPSi binds to the metallic oxides with a stable covalent binding even when the polymerization of MPC was carried out. This MPSi (and/or poly(MPC-*co*-MPSi)) layer(s) and the Co-Cr-Mo substrate might contribute to the stable polymer/metal interface.[55]

The coefficients of dynamic friction of various bearing couples obtained in previous studies are summarized in Table I. In Figure 8, the Co-Cr-Mo/Co-Cr-Mo couple shows a friction coefficient of $\sim$0.19, which is as high as that described in previous studies.[36,56] The CLPE/Co-Cr-Mo couple also shows a friction coefficient of $\sim$0.14, as high as that described in previous studies.[36,57,58] In contrast, the Co-Cr-Mo-*g*-MPC surface with respect to each material shows an extremely low friction coefficient when compared with that of the untreated Co-Cr-Mo surface. As MPC is highly hydrophilic and poly(MPC) is water soluble, the water contact angle of the Co-Cr-Mo-*g*-MPC surface was lower than that of the untreated Co-Cr-Mo surface, as shown in Figure 5. Consequently, the grafted poly(MPC) layer successfully provided high lubricity in the form of "surface gel hydration lubrication" to the Co-Cr-Mo surface (Fig. 8).[59]

TABLE I
Coefficients of Dynamic Friction of Various Bearing Couples in Previous Studies

Bearing Couple			
Pin	Disc or Plate	Friction Coefficient	Reference
Co-Cr-Mo	Co-Cr-Mo	0.19–0.27	36, 56
UHMWPE	Co-Cr-Mo	0.05–0.13	36, 57, 58
CLPE-*g*-MPC	MPC "grafted to" Co-Cr-Mo	0.07–0.13	36
Cartilage	Stainless steel	0.01–0.05	61
Cartilage	Cartilage	0.02	62

Various factors such as the type of bearing material, surface roughness, homogeneity of the surface, and chemical composition affect the lubricity of artificial joints.[60] In Figure 8, the friction coefficient of the CLPE/Co-Cr-Mo-*g*-MPC couple was greater than that of Co-Cr-Mo/Co-Cr-Mo-*g*-MPC couple ($p <$ 0.001 in both 10 and 100 cycles). The significant difference for the friction coefficient of those bearing couples was probably attributed to a surface roughness of bearing pin: although the bearing surface of Co-Cr-Mo pins was polished so that the average surface roughness (R_a) was $\sim$0.01 μm, the bearing surface of CLPE pins was only machine-finished so that the R_a was $\sim$20 μm. These bearing surfaces were actually comparable with those of femoral ball and acetabular cup products, respectively. However, if the bearing surface of CLPE pins was polished or direct molded like that of Co-Cr-Mo pins, the friction coefficient of the CLPE/Co-Cr-Mo-*g*-MPC couple would be similar to that of Co-Cr-Mo/Co-Cr-Mo-*g*-MPC couple.

In the case of Co-Cr-Mo-*g*-MPC, the lubricity changes depending on the ambient *in vitro* and *in vivo* conditions. The previous study reported that the hydrogel cartilage surface is assumed to have a brush-like structure: a part of the proteoglycan ag-