送信先 FAX:075-751-8409
TKA / UKA 登録フォーム (2007/1/18 版)

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I 病院、術者と患者

ARJ 登録病院：_____

執刀医イニシャル：(姓)_____(名)_____　指導医イニシャル：(姓)_____(名)_____

(事前登録したイニシャルを記入)

(執刀医とは手術を主に行った医師、指導医とは執刀医と同等以上の経験があるもので、執刀医の指導にあたった医師)

(執刀医、指導医が事前登録していなければ、このフォームを提出と同時に登録する)

患者 ID：(同意書に記入されたものを参照すること)

1. 生年月日 (西暦)：_____年_____月 _____日生　2. 性別：(男 ・ 女)
3. 名前 (名前の最初の文字：山田太郎ならば名前の「たろう」の「た」を記入、名字ではないので注意)：___
4. 生まれた場所 (都道府県名、海外であればその国名を記入：愛知県、中国など)：_____
5. 登録病院 ID:_____

II 初回 TKA/UKA

1. 手術年月日 (西暦)：_____年_____月_____日
2. 手術側： 右 / 左　(両側同日の場合、2枚作成する)
3. 既往手術：なし / HTO 後 / 鏡視下手術後 / その他 _____　UKA の場合 (内側・外側)
4. 手術診断名：OA / RA または RA 類似疾患 / ION / 外傷 / シャルコー関節/ その他 _____

III 再手術 TKA/UKA　(再手術とはいかなる理由でもインプラントを抜去または入れ換えした場合とする)

1. 初回手術時について (この項目は、可能であれば記載する)
   初回手術年月日 (西暦)：_____年 _____月 _____日 初回手術施設名：_____
   初回手術診断名：OA / RA または RA 類似疾患 / ION / 外傷 / シャルコー関節/その他 _____
2. 今回の手術年月日 (西暦)：_____年_____月_____日
3. 手術側： 右 / 左　(両側同日の場合、2枚作成)
4. 手術回数 (今回の手術を含める)：(1、2、3、4、それ以上_____回 および 不明)
5. 手術の理由：loosening (大腿骨・脛骨・膝蓋骨) / 感染 / 脱臼・instability / インプラント破損 (大腿骨・脛骨・膝蓋骨) /ポリエチレン摩耗 (脛骨・膝蓋骨) / 外傷 / 可動域制限 / その他 _____
6. 手術の内容：抜去のみ (大腿骨抜去 / 脛骨抜去 / 膝蓋骨抜去 / insert 抜去)　再置換 (大腿骨・脛骨・膝蓋骨・insert)　抜去したインプラント商品名：_____

IV 手術手技

1. 手術時間：_____時間_____分
2. アプローチ：para-patella / mid-vastus / sub-vastus / lateral / QS
3. minimally invasive technique：なし / あり　4. navigation system：非使用 / 使用
5. 膝蓋骨置換：非置換 / 置換　6. セメント： なし / あり / hybrid ～ 使用部分 (大腿骨・脛骨・膝蓋骨)
7. 抗生剤含有セメント：なし / あり (_____[抗生剤名]を _____グラム/ セメント1パック)
8. 骨移植：なし / 一部あり (自家・同種) (大腿骨・脛骨・膝蓋骨) / あり (自家・同種) (大腿骨・脛骨・膝蓋骨)
9. 生体活性材料 (人工骨など) の使用： なし / 一部あり (大腿骨・脛骨・膝蓋骨) / あり (大腿骨・脛骨・膝蓋骨)：商品名_____
   (一部ありは cyst や小欠損に対する骨移植、ありは明らかな骨欠損に対する骨移植や impaction bone graft など)
10. 補強部品： なし / あり (augmentation、long stem、その他_____)

該当項目に○、下線部へは記入

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2

ARJ 登録病院：_____

患者生年月日 (西暦)：_____年 _____月 _____日 手術側：右 / 左 (両側同日の場合、2枚作成する)

(FAX 時の1枚目と2枚目の文書が同一患者のものであることを確認するために必ず記入すること)

V COMPONENT LABEL の添付

大腿骨側

スクリュー

脛骨側

ベースプレート

生体活性材料

インサート

補強部品

膝蓋骨側

その他

セメント

該当項目に○、下線部へは記入

別紙４

研究成果の刊行に関する一覧表レイアウト

雑誌

発表者氏名	論文タイトル名	発表誌名	巻号	ページ	出版年
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Kyomoto M, Moro T, Miyaji F, Hashimoto M, Kawaguchi H, Takatori Y, Nakamura K, Ishihara K	Effects of mobility/immobility of surface modification by 2-methacryloyloxyethyl phosphorylcholine polymer on the durability of polyethylene for artificial joints.	***J Biomed Mater Res A***			in press.
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Kyomoto M, Moro T, Iwasaki Y, Miyaji F, Kawaguchi H, Takatori Y, Nakamura K, Ishihara K	Super-lubricious surface mimicking articular cartilage by grafting poly(2-methacryloyloxyethyl phosphorylcholine) on orthopaedic metal bearings.	***J Biomed Mater Res A***			in contribution.
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Photo-immobilization of a phospholipid polymer for surface modification

Tomohiro Konno[a,b], Hirokazu Hasuda[a], Kazuhiko Ishihara[b], Yoshihiro Ito[a,*]

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Abstract

A photo-reactive polymer having a phospholipid polar group was prepared, and the polymer was photo-immobilized on polymeric surfaces, where its interactions with biocomponents were investigated. By using a photo-immobilization method, the polymer was used for surface modification of polyethylene and polypropylene, polymers whose surfaces were not treated in our previous development of the phosphorylcholine-derived polymer. The photo-reactive polymer was synthesized by a coupling reaction involving copolymer consisting of 2-methacryloyloxyethyl phosphorylcholine and methacrylic acid with 4-azidoaniline. When the polymer was unpattern immobilized on the surface, X-ray photo-electron spectroscopic analysis and static contact angle measurements were performed. It was shown that the surface was covered with phospholipid polar groups. Micropattern immobilization was carried out using a micropatterned photo-mask. Measurements using atomic force microscopy showed that the swelled micropatterned polymer was five times as thick as the dried one. Protein adsorption and platelet adhesion were reduced on the polymer-immobilized regions. Mammalian cells did not adhere, and formed aggregates on the immobilized regions. In conclusion, the photo-reactive phospholipid polymer was covalently immobilized on the conventional polymer surfaces and it tended to reduce interactions with proteins and cells.

Keywords: Photo-immobilization; Phospholipid polymer; Surface modification; Protein adsorption; Cell adhesion

1. Introduction

Lipid membranes are used as biomimetic systems, and are expected to become a key component of novel biomolecular materials [1–14]. In particular, lipid bilayer membranes on solid supports have been the subject of numerous publications [1–11]. The membranes prepared on various solids by optimized variations of the available deposition chemistries have been shown to accommodate a variety of proteins and enzymes in controlled orientations and in active conformations. The supported lipid bilayer is considered to mimic the native environment of membrane-associated biomolecules. These membranes are also promising surfaces for developing new biosensors and coating materials that resist non-specific interactions with proteins and cells.

The lipid head group of phosphorylcholine, a zwitterion, is a common group in the lipid molecules that form biological membranes, and is considered to play an important role as a surface material for biomedical devices by reducing interaction with proteins and cells. As a biomimetic polymer, 2-methacryloyloxyethyl phosphorylcholine (MPC)-containing polymer was synthesized by the group of Ishihara and Nakabayashi [15,16]. The polymer shows non-thrombogenicity, that is, suppression of non-specific protein adsorption, platelet adhesion, activation, and aggregation when the polymer contacted whole blood, even in the absence of anticoagulants.

Recently, some types of MPC-containing copolymers have been synthesized for coating [17] and covalent immobilization was achieved [18–20]. However, the

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covalent immobilization was limited to specialized surfaces. Therefore, in the present investigation, photo-immobilization was employed for covalent immobilization of the polymer on a broader variety of surfaces.

In addition, although many synthetic polymers have been devised to improve surface reducing interaction with proteins or cells, it is difficult to directly compare the surface properties of different polymers under precisely the same conditions. Therefore, a micropatterning method has been devised for lipids and polymers [21–23], and the method has proved useful for comparing the interaction of polymers with proteins and cells [24–26]. We modified the method of Matsuda and Sugawara [27], and have applied this method to some growth factors [28–30], sulfated hyaluronic acid [31], heparin [32], and thermo-responsive polymer [33]. In the present study, micropatterning of MPC polymer was performed, and the interactions with proteins and cells were investigated.

2. Materials and methods

2.1. Synthesis of photo-reactive MPC polymer

The polymer synthesis is illustrated in Fig. 1. MPC copolymer consisting of MPC (90 mol%) and methacrylic acid (10 mol%) was obtained from NOF Co. Ltd. (Tokyo, Japan), and is referred to as PMAc. The molecular weight of PMAc, as measured by gel permeation chromatography, was 2.2×10^5. Modification of PMAc was performed as follows: 4-azidoaniline (12.44 mg) and water-soluble carbodiimide (17.47 mg) were dissolved in 2 ml of PMAc solution (5 wt%) and 98 ml of water was added to the solution. The solution was left to stand for 24 h. After the reaction, the product was dialyzed with dialysis cassette (PIERCE, Rockford, IL) until no further release of azidoaniline through the cassette was confirmed by ultraviolet (UV) absorption. The resultant solution was freeze-dried. The azidophenyl-derivatized PMAc is referred to as Az-PMAc. Elemental analysis indicated that the amount of azidophenyl group in Az-PMAc was 6%.

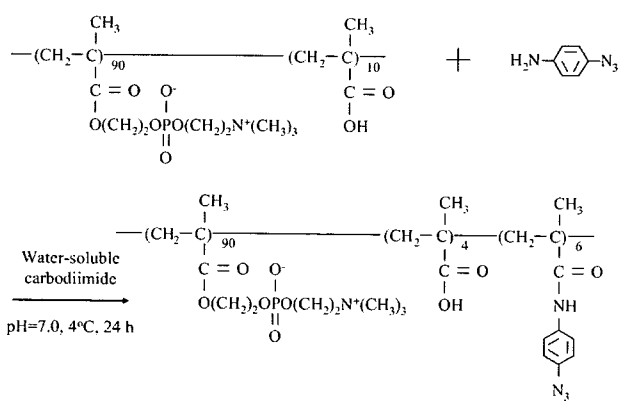

Fig. 1. Synthetic scheme for photo-reactive phosphorylcholine-containing polymer.

2.2. Micropatterning

The micropatterning method is illustrated in Fig. 2. An aqueous solution of Az-PMAc (1 wt%) was cast on polyethylene and polypropylene plates (diameter 22 mm), which were purchased from Sarstedt (Newton, NC) and from Nikkyo Technos Co. Ltd. (Tokyo, Japan), respectively, and air-dried at room temperature. Subsequently, the plate was covered with a photo-mask, which was manufactured by Toppan Printing Co. Ltd. (Tokyo, Japan) and was UV-irradiated with a UV lamp (UV Spot Light Source L5662, Hamamatsu Photonics, Hamamatsu, Japan) from a distance of 5 cm for 10 s ($16\,mW/cm^2$). When an unpatterned surface was prepared, the photo-mask was not employed. The plate was then repeatedly washed with distilled water.

2.3. Measurement of contact angle

The unpatterned sample was placed on the holder of a CA-W Automatic Contact Angle Meter (Kyowa Interface Science Co. Ltd., Saitama, Japan) and a drop of water (0.4 μl) was put on the sample surface. The contact angle of the drop on the surface was measured at room temperature. At least 10 contact angles on different areas were measured and averaged.

2.4. Measurement by X-ray photo-electron spectroscopy (XPS)

The unpatterned sample was inserted in the holder of an XPS, AXIS-HSi (Shimadzu/Kratos, Kyoto, Japan). After evacuation, the measurement was carried out under 3×10^{-9} Torr. The X-ray source was CuK_α, the applied voltage was 12 kV, and the electric current was

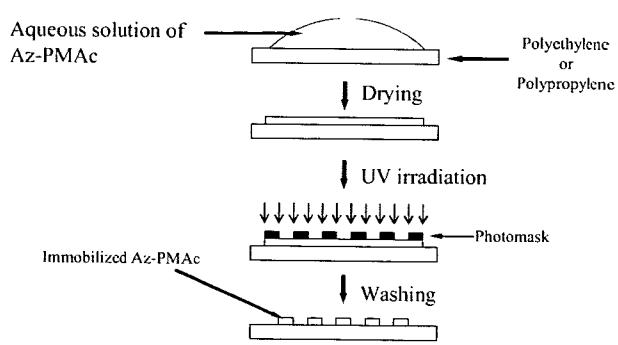

Fig. 2. Schematic illustration of micropatterning procedure.

10 mA. The take-off angle of the photo-electrons was 90°.

2.5. Measurement by atomic force microscopy (AFM)

The measurement was performed using an SPI-3800 (Seiko Instruments Inc., Chiba, Japan). The micropatterned sample was dried in vacuo for 1 day at room temperature and was set in a cell holder into which water could be injected. After observation of the dry sample, distilled water was injected into the sample cell and the same position was observed. The measurement was performed using the tapping mode with a nominal force constant of 0.09 N/m.

2.6. Interaction with proteins

Fluorescein isothiocyanate (FITC)-labeled bovine serum albumin and FITC-labeled immunoglobulin were purchased from Sigma (St. Louis, MO). FITC-labeled fibrinogen was prepared as follows: a phosphate-buffered solution (PBS; 25 ml) containing human fibrinogen (500 μg) was added dropwise to a PBS (25 ml, pH 8.0) containing FITC (12.5 μg) and the pH of the mixture was adjusted to 9.0. The mixture was stirred at room temperature for 2 h. The resulting solution was dialyzed against double-distilled water using a Millipore dialysis tube (cut-off less than 10 000) at 4°C until the release of FITC became undetectable by fluorescence spectroscopy. Finally, the purified protein was lyophilized. All procedures were carried out in darkness.

The protein adsorption experiment was performed as follows: the sample plates were incubated in PBS containing the FITC-labeled albumin (10 mg/ml), FITC-labeled immunoglobulin (2 mg/ml), or the FITC-labeled fibrinogen (10 mg/ml) at 37°C for 10 min. After being washed with PBS, the sample was observed by fluorescence microscopy.

2.7. Interaction with platelets

Human whole blood was collected from healthy volunteers in a disposable syringe containing 3 ml of aqueous solution of 3.8 wt% sodium citrate. The citrated whole blood was immediately centrifuged for 15 min at 1200 rpm to obtain citrated platelet-rich plasma (PRP). The micropatterned sample plates were placed in contact with PRP and left for 60 min at 37°C. The PRP was removed with an aspirator, and the membrane was rinsed three times with PBS. Subsequently, 2.5 vol% glutaraldehyde in PBS was poured into each well containing the sample plates, and the samples were stored at room temperature for 2 h in order to fix the blood components on the sample plate. After it had been rinsed sufficiently with distilled water, the samples were freeze-dried. The surface of the sample plate was observed with a scanning electron microscope (SEM) after gold-sputtering treatment.

2.8. Cell culture

RAW264 (originating from leukemic mouse monocytes) cells were purchased from Riken Cell Bank (Tsukuba, Japan) and were cultured in minimum essential medium (Sigma, St. Louis, MO) with 10% fetal bovine serum and 1% non-essential amino acids (Invitrogen Life Technologies, Carlsbad, CA). The recovered cells were washed with the culture medium and suspended in each medium containing no serum (3×10^5 cells per 60 mm-diameter culture dish). The cell suspension was added to the sample plate, which was sterilized with 70% ethanol. The cells were incubated at 37°C under 5% v/v of CO_2 and were observed by a phase-contrast microscope equipped with a video camera.

3. Results and discussion

3.1. Synthesis of photo-reactive MPC polymer

The UV and fluorescence spectra of Az-PMAc are shown in Fig. 3. In the UV spectrum of the photo-reactive polymer, an absorption at 269 nm, which is assignable to the azidophenyl group, was observed.

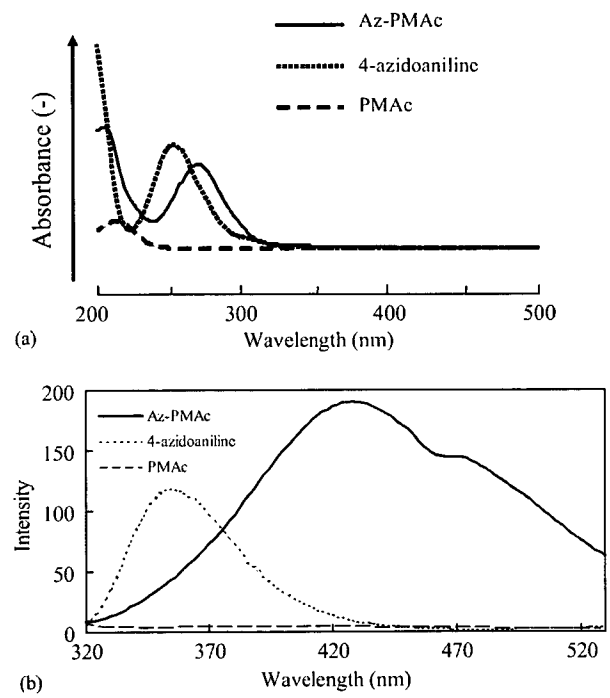

Fig. 3. UV (a) and fluorescence (b) spectra of azidoaniline, PMAc, and Az-PMAc.

Fig. 3a indicates that the absorption was slightly red shifted from the corresponding absorption of 4-azidoaniline, and Fig. 3b shows that the fluorescence was red shifted. These shifts may be due to electron delocalization of the azidophenyl group caused by amide bond formation. In previous studies, the peaks of photo-reactive hyaluronic acid and photo-reactive heparin were also red shifted from 4-azidoaniline [35,37].

3.2. Photo-immobilization

The Az-PMAc was coated on the plates and the coated surface was UV-irradiated with a photo-mask (Fig. 4). The surface pattern was the same as that of the photo-mask. The micropatterned surface was observed by phase-contrast microscopy (Fig. 4b) and by fluorescence microscopy (Fig. 4c). It is known that azido groups are decomposed by UV irradiation, and nitrene groups, which are highly reactive radical groups, are produced. The cast Az-PMAc formed molecular networks as a result of the produced radical groups. In addition, a micropatterned surface was formed both on polyethylene (Fig. 4c) and polypropylene (Fig. 4d) plates. The present result demonstrates that photo-immobilization is useful for covalent immobilization of MPC on various materials.

Previously, Prucker et al. [34] reported photo-chemical attachment of polymer films to solid surfaces via benzophenone derivatives. In their case, the amount of immobilized polymer on the surface reached saturation after about 10–20 min, when the light intensity was 100 mW/cm^2. In the present study, 10 s were enough for preparation of micropatterned immobilization, although the intensity was 16 mW/cm^2. Although the strength of binding of immobilized polymer to the surface has not been investigated, it was demonstrated that 10 s was enough for washing out of non-bound polymers.

The unpatterned PMAc surface on the polyethylene plate was made by UV-irradiation without a photo-mask. XPS measurement of the unpatterned surface demonstrated that the surface was covered with phospholipid polar groups (Fig. 5). In addition to the XPS spectrum of the previously reported MPC polymer coating surface [35,36], a new peak that was ascribed to the amide bond formed by reaction between PMAc and azidoaniline was found at 398 eV.

The water contact angle was measured on the unpatterned surface (Fig. 6). The contact angle on the

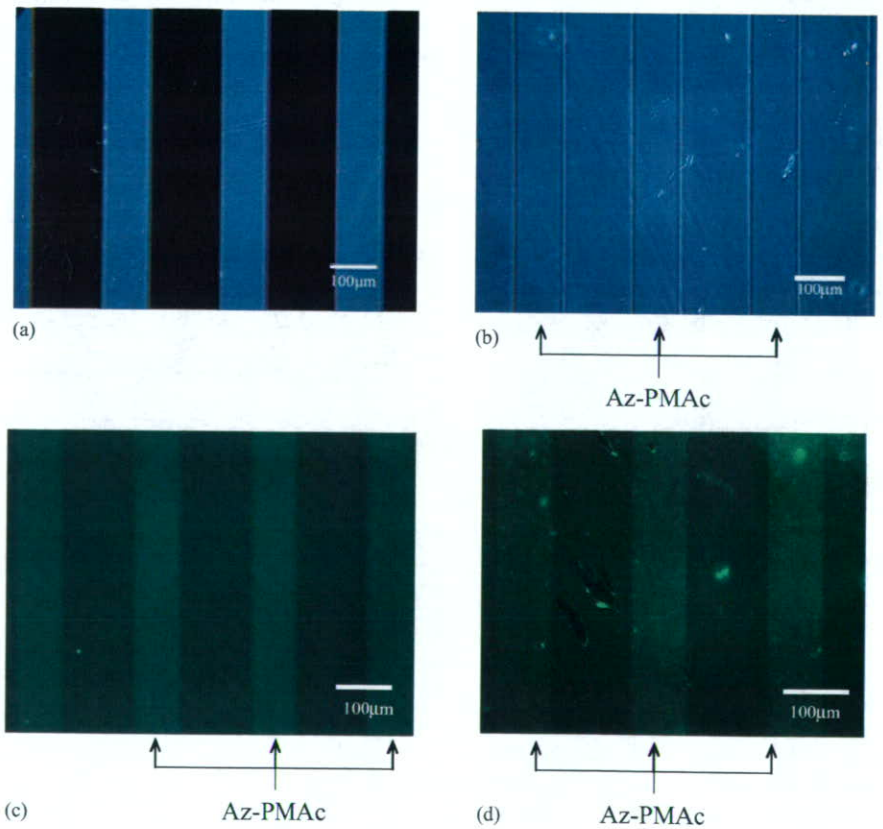

Fig. 4. Phase-contrast micrographs of photo-mask (a); and micropatterned surface of the polyethylene plate (b); fluorescence micrographs of micropatterned surface of the polyethylene plate (c); and of the polypropylene plate (d).

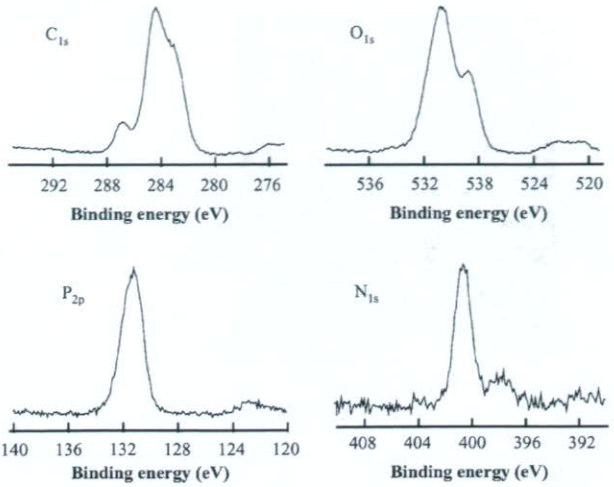

Fig. 5. XPS spectra of the Az-PMAc immobilized polyethylene surface.

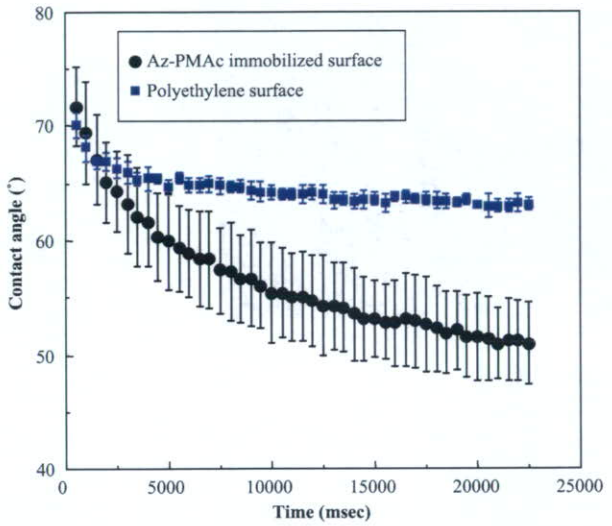

Fig. 6. Time course of static contact angle of water on the Az-PMAc-immobilized and non-immobilized polyethylene surface.

PMAc-immobilized surface rapidly decreased with time, although that on the polyethylene surface did not. It was demonstrated that a hydrophilic surface was formed by immobilization of the PMAc.

The surface was observed by AFM, as shown in Fig. 7. In the dried state, the thickness was about 800 nm. However, the PMAc layer rapidly swelled in water to a thickness of about 4000 nm. The hydrogel state of PMAc was formed after soaking for 10 min in water. Fig. 8 shows the force curves of the micropatterned surface. On the surface of bare polyethylene (2, 4, 6, 8, 10), the force abruptly increased with decreasing distance between the cantilever and the surface. On the other hand, on the Az-PMAc-immobilized region (1, 3,

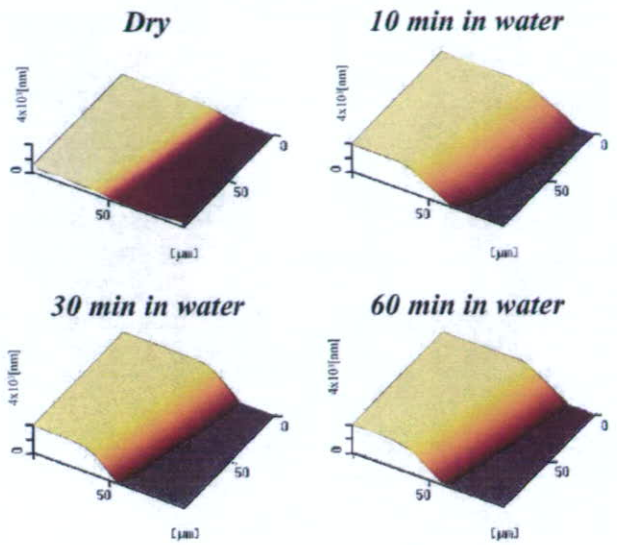

Fig. 7. AFM images of the Az-PMAc-micropatterned surface. The dried sample was measured and then incubated in water for different periods.

5, 7, 9) the force did not increase so abruptly with the decrease of distance. These results demonstrated that the Az-PMAc surface was so soft that force was not significantly produced on the surface.

3.3. Interaction with biological components

The sample plate was immersed in the protein solutions, and the protein-adsorbed sample was observed by fluorescence microscopy (Fig. 9). Albumin, immunoglobulin, and fibrinogen predominantly adsorbed onto the non-immobilized surface. The fluorescence intensity of adsorbed proteins is significantly higher than that of Az-PMAc alone. Previously, we reported that an MPC-adsorbed surface inhibited adsorption of proteins [37,38]. The present study confirmed the previous reports.

Human blood platelet adhesion onto the micropatterned surface was observed by SEM. The number of platelets on the PMAc-immobilized regions $(0.34 \pm 0.02) \times 10^3\,\text{cell}/\mu\text{m}^2$ was significantly less than that on the non-immobilized regions $(1.13 \pm 0.12) \times 10^3\,\text{cell}/\mu\text{m}^2$. The non-adhesiveness of MPC polymer has been reported previously [38]. The present study critically demonstrated this property.

The time course of behavior of RAW264 on the micropatterned surface is shown in Fig. 10. When the cells were added to the surface, they randomly distributed independent of the immobilized material. However, after 5 min, they began to aggregate on the Az-PMAc-immobilized surface; the cellular aggregates increased in size with time and eventually floated. On the

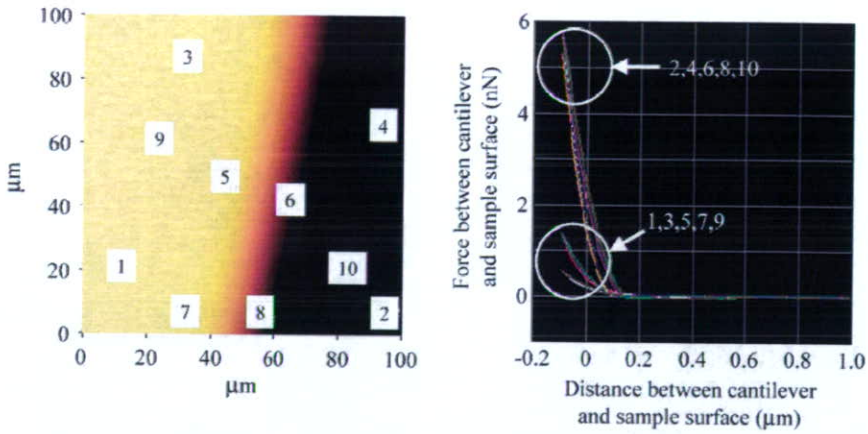

Fig. 8. Contact points of the cantilever with surfaces and the force curve between the cantilever and surfaces. The numbers represent the contact points of the cantilever. Points 1, 3, 5, 7, and 9 were on the Az-PMAc-immobilized surface and points 2, 4, 6, 8, and 10 on the bare polyethylene surface.

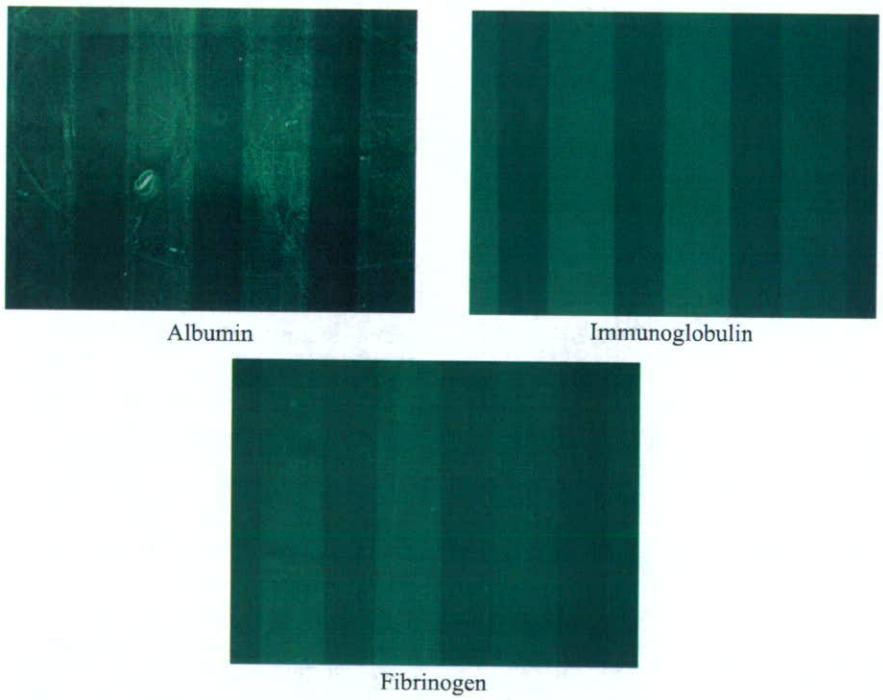

Fig. 9. Fluorescence micrographs of proteins (albumin, immunoglobulin, and fibrinogen) adsorbed onto the Az-PMAc-micropatterned polyethylene surface. The wavelengths of excitation and emission were 470 ± 20 and 525 ± 25 nm, respectively.

non-immobilized region the cells adhered and spread on the surface. The floated aggregates on the Az-PMAc-immobilized region were completely removed by mild shaking. It is known that RAW264 shows macrophage-like properties and tends to adhere to various materials [39]. It was demonstrated that PMAc inhibited the adhesion of even very adhesive cells.

The present study demonstrated photo-immobilization of a phospholipid polymer and visualized the interactions with biocomponents such as proteins, platelets, and cells. The photo-immobilization technique is useful for surface modification and the phospholipid polymer significantly reduced the interactions with proteins and cells.

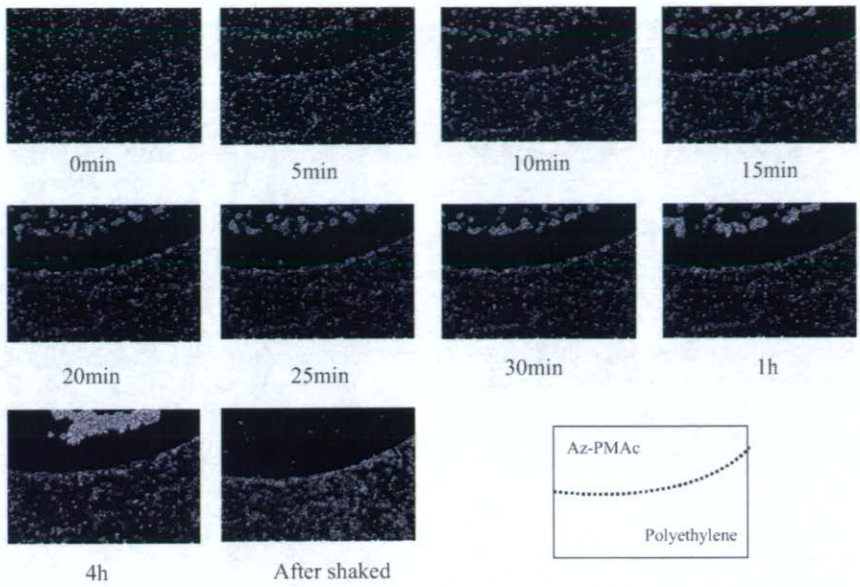

Fig. 10. Time course of behavior of RAW264 cells on Az-PMAc-immobilized and non-immobilized region (polyethylene surface), as observed by phase-contrast microscopy with a video camera.

Acknowledgements

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Enhancement of mechanical strength of TiO_2/high-density polyethylene composites for bone repair with silane-coupling treatment

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Abstract

Mechanical properties of composites made up of high-density polyethylene (HDPE) and silanated TiO_2 particles for use as a bone-repairing material were investigated in comparison with those of the composites of HDPE with unsilanized TiO_2 particles. The interfacial morphology and interaction between silanated TiO_2 and HDPE were analyzed by means of Fourier transform infrared (FT-IR) spectroscopy and scanning electron microscopy (SEM). The absorption in spectral bands related to the carboxyl bond in the silane-coupling agent, the vinyl group in the HDPE, and the formation of the ether bond was studied in order to assess the influence of the silane-coupling agent. The SEM micrograph showed that the "bridging effect" between HDPE and TiO_2 was brought about by the silane-coupling agent. The use of the silane-coupling agent and the increase of the hot-pressing pressure for shaping the composites facilitated the penetration of polymer into cavities between individual TiO_2 particles, which increased the density of the composite. Therefore, mechanical properties such as bending yield strength and Young's modulus increased from 49 MPa and 7.5 GPa to 65 MPa and 10 GPa, respectively, after the silane-coupling treatment and increase in the hot-pressing pressure.

Keywords: A. Composites; C. Infrared spectroscopy; D. Mechanical property

1. Introduction

Since the discovery of Bioglass® in the early 1970s [1], various bioactive ceramics, including sintered hydroxyapatite [2] and glass–ceramic A-W containing crystalline apatite and wollastonite ($CaO{\cdot}SiO_2$) [3], have been developed and clinically used as materials, for example, for artificial middle-ear bones, maxillofacial implants, bone fillers, artificial iliac crests, artificial vertebrae, and artificial intervertebral discs. Among them, glass–ceramic A-W shows fracture toughness as high as 2 MPa $m^{1/2}$ [4,5] and high bioactivity [6]. Hence it can be used to replace bones subjected to high loads, such as vertebrae and intervertebral discs [7]. Highly loaded bones such as tibial and femoral bones, however, cannot be replaced even with this glass–ceramic, since its fracture toughness is lower and its elastic modulus is higher than those of natural bone. For these purposes, implants made of metal, such as titanium metal and

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its alloy, subjected to alkali and heat treatment [8] or alkali, water and heat treatment [9] have been developed. They have, however, much higher elastic moduli than that of natural bone. This is a critical problem in some applications, since the high elastic modulus of these materials may induce resorption of the surrounding bone because of stress shielding. Therefore, highly bioactive materials with mechanical properties analogous to those of natural bone are desired to be developed.

Hydroxyapatite-particle-reinforced high-density polyethylene (HDPE) composite (HAPEX®) was developed in the early 1980s as an analogue for bone [10]. It is already in clinical use as the material of artificial middle-ear bones. Some of the mechanical properties of HAPEX®, such as the tensile strength, have already been confirmed to be suitable for use in the human body [11–13]. However, the fracture toughness and elastic modulus of HAPEX® are lower than those of living bone. Glass–ceramic A-W-reinforced HDPE has been in development since 1998 [14,15]. The bioactivity of this composite is higher than that of HAPEX®, but the mechanical strengths of this composite are lower.

Previous studies by the present authors have shown that TiO_2-nanoparticle-reinforced HDPE composites (hereafter TiO_2/HDPE) exhibit bending strength and Young's modulus analogous to those of natural bone as well as bioactivity [16,17]. The bending strength and Young's modulus were found to vary from almost 28 to 54 MPa and 1.4 to 7.6 GPa, respectively, depending on the TiO_2 content. However, only a very weak mechanical adhesion seemed to exist between constituent phases in these composites. The fracture surface of the TiO_2/HDPE composites showed no residual HDPE on the TiO_2 particles, indicating that no chemical bond existed between TiO_2 and HDPE. Also, there were voids at the particle–matrix interface, resulting in a lower density than the theoretical one.

For incompatible composites containing at least one component, the final mechanical strengths are determined by two competing factors. One is the extent of compatibility between the inorganic filler and the polymer. The other is the presence of voids, cracks and fractures in the interphase between the filler and polymer [18].

The interface between inorganic filler particles and the matrix polymer plays an important role in determining the properties of a composite. Particle–matrix interaction is expected to influence the structure of the composites, mainly through its influence on the dispersion of the filler particles in the matrix [19–21]. Most commonly, the surface of the filler is treated to become more chemically compatible with the polymer matrix. A very common reactive treatment is silane treatment of the fillers [22]. The widespread use of silane treatment can be attributed to the availability of a wide range of endgroups. Thus, the interaction between the inorganic surface and the matrix polymer can be tuned by selecting the appropriate endgroups.

In this work, we focus on the study of composites of HDPE and surface-modified TiO_2, in particular, the adhesion between the two phases. The silane molecule used for surface treatment has the hydrocarbon functional group. The hydrocarbon endgroup is used in coupling agents that interact well with polyolefin, such as polyethylene. Also, the synergistic effects of surface treatment and of the increase of hot-pressing (HP) pressure applied during shaping on mechanical strength were investigated.

2. Experimental

2.1. Materials

Solvents and reagents, all of special reagent grade, were used without further purification. The anatase-type TiO_2 nanopowder was manufactured by Ishihara Sangyo Kaisha, Ltd., Mie, Japan. The median particle size of TiO_2 powders was 535 nm [17]. TiO_2 powders were treated with a silane-coupling agent as follows: 1.1 g of [γ-(methacryloxy)propyl]trimethoxysilane (γ-MPS) (Shinetsu Co. Ltd., Osaka, Japan), 1.6 g of ethanol and 0.2 g of ion-exchanged distilled water were stirred with a magnetic stirrer for 10 min. The solution containing the silane-coupling agent was added to 110 g of TiO_2 powder and mixed in the shaker mixer TURBULA T2F (W. A. Bachofen AG Co., Basel, Switzerland) at 25 °C for 1 h. The rotation speed was 96 rpm. After mixing, the mixtures were dried and heated at 130 °C for 5 min.

HDPE (Japan Polyolefins Co., Ltd., Tokyo, Japan) has the number-average molecular weight (Mn) of 1.21×10^4, weight-average molecular weight (Mw) of 7.67×10^4 and z-average molecular weight (Mz) of 47.6×10^4; Mw/Mn is 6.35 and Mz/Mw is 6.20. The melt flowing rate (MFR) of this polyethylene is 8.

The influence of silanation of TiO_2 nanoparticles on the flow behavior of TiO_2/HDPE compound was evaluated using a computer-controlled torque rheometer, 30C-150 (Toyo Seiki Seisaku-sho, Ltd., Tokyo, Japan). Reaction was performed in a chamber with continuous monitoring of torque. The mixer chamber was initially heated to 210 °C.