



Construction of a blood-compatible interface based on surface segregation in a polymer blend



Toyoaki Hirata ^a, Hisao Matsuno ^{a, **}, Daisuke Kawaguchi ^b, Norifumi L. Yamada ^c, Masaru Tanaka ^{d, 1}, Keiji Tanaka ^{a, e, *}

^a Department of Applied Chemistry, Kyushu University, Fukuoka 819-0395, Japan

^b Education Center for Global Leaders in Molecular Systems for Devices, Kyushu University, Fukuoka 819-0395, Japan

^c Neutron Science Laboratory, High Energy Accelerator Research Organization, Ibaraki 305-0801, Japan

^d Department of Biochemical Engineering, Yamagata University, Yamagata 992-8510, Japan

^e International Institute for Carbon-Neutral Energy Research (WPI-I2CNER), Kyushu University, Fukuoka 819-0395, Japan

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ABSTRACT

The technique of surface segregation was applied to prepare a bio-inert polymer interface. A small amount, 10 wt%, of poly(2-methoxyethyl acrylate) (PMEA), which exhibits excellent bio-inertness properties, fed into a matrix polymer was able to suppress platelet adhesion sufficiently to be of practical use. PMEA was effective because it was preferentially segregated at the outermost region of the polymer blend. Combining interfacial-sensitive analyses such as the air bubble contact angle and neutron reflectivity measurements and sum-frequency generation spectroscopy with the platelet adhesion test gives a better understanding of how the bio-inert property is expressed at the water interface.

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1. Introduction

Surface functionalization is of growing interest for many industrial and medical applications to enhance the value of the materials used in these fields. Thus, various chemical and physical methods to optimize surface properties have been proposed [1–16]. Blending different kinds of polymers is one such technology [4–12]. When a polymer “A” with a lower surface free energy is mixed into a different polymer “B”, “A” is preferentially partitioned into the surface. This phenomenon is called surface segregation [4–12]. Thus, if polymer “A” possesses a special function, the surface property of polymer “B” is consequently modified. This method of surface modification is quite simple and does not need special apparatus unlike other methods such as chemical reaction [1–3,13,14], corona [15,16] and plasma treatment [17,18]. The most

intriguing advantage of this method is that the surface so modified is more robust because the surface segregation is driven by thermodynamics. In addition, this technique can be applied to a valuable polymer because even though a small amount of the polymer is fed into a matrix polymer, it should all be concentrated at the surface.

Previously, we applied this method to prepare a thin film, in which the outermost region was fully covered with poly(2-methoxyethyl acrylate) (PMEA) [19], a typical bio-inert polymer [20–22]. Although PMEA is in a rubbery state under physiological conditions due to its low glass transition temperature (T_g), a sufficiently stable and flat PMEA surface could be constructed by adding a polymer known to be glassy, poly(methyl methacrylate) (PMMA) [19]. The enrichment of PMEA even took place at the interface with water. Using various techniques to measure interfacial-sensitivity, we have succeeded in gaining a better understanding of aggregation states and interfacial dynamics of PMEA at the water interface and learning more about the effects of the aggregation states on the bio-inert properties of PMEA [23,24]. In previous studies, the blend ratio of PMEA to PMMA was set at 50/50 (wt/wt) to ensure perfect coverage with PMEA at the outermost water interface [19,23,24]. Here, we show that a small amount of PMEA, 10 wt%, fed into PMMA was sufficient to exhibit bio-inertness at a level of practical use to enable platelet adhesion.

* Corresponding author. Department of Applied Chemistry, Kyushu University, Fukuoka 819-0395, Japan.

** Corresponding author. Department of Applied Chemistry, Kyushu University, Fukuoka 819-0395, Japan.

E-mail addresses: h-matsuno@cstf.kyushu-u.ac.jp (H. Matsuno), k-tanaka@cstf.kyushu-u.ac.jp (K. Tanaka).

¹ Present address: Institute for Materials Chemistry and Engineering, Kyushu University, Fukuoka 819-0395, Japan.

2. Experimental section

2.1. Materials

Polydisperse PMEA at a quality level that can be produced at the industrial scale for use in medical applications was synthesized by free-radical polymerization [19]. Commercially-available mono-disperse PMMA and deuterated PMMA (dPMMA) synthesized by living anionic polymerization were used. Characteristics of the polymers determined by gel permeation chromatography (GPC) and differential scanning calorimetry (DSC) are summarized in Table 1.

2.2. Film preparation

Thin PMEA/PMMA and PMEA/dPMMA blend films with a thickness of approximately 60 nm were prepared onto SiO_x substrates. The blend ratio of PMEA/(d)PMMA was adjusted to a weight ratio of 10/90 (wt/wt). These films were dried in a vacuum oven at room temperature for 24 h and subsequently annealed for 6 h at 413 K which was above the T_g of 375 (377) K calculated based on the Fox equation [25] and below the phase separation temperature of 457 (456) K calculated based on the Flory–Huggins equation [26] for PMEA/(d)PMMA blends. Phase separation did not occur for these blend films containing 10 wt%-PMEA at the temperatures employed. That is, the system was always miscible as previously reported [19].

2.3. Atomic force microscopic (AFM) observations

The surface morphology of the blend films was examined by AFM (Agilent Technologies 5500 Scanning Probe Microscope, Agilent Technologies, Inc., Santa Clara, CA, US) using an intermittent contact mode at room temperature in water. The cantilever tip used for the measurement was microfabricated from Si, and its spring constant and resonance frequency in air were 2.8 N·m⁻¹ and 75 kHz, respectively. The tip radius was approximately 5 nm. The drive frequency used in water was 30 kHz, which was on the lower frequency side of the resonance. To avoid possible deformations of the sample surface during the observation, the ratio of the set point to the free amplitude of the cantilever was maintained at approximately 0.9 (10% damping of the amplitude of oscillation).

2.4. Contact angle measurements

The blend films were characterized at the water interface by static contact angle (θ) measurements at room temperature using an air bubble as a probe. The θ value was recorded as a function of the immersion time in water using a Drop Master 500 (Kyowa Interface Science Co. Ltd., Saitama, Japan). The first θ value was obtained immediately after film immersion into water, and the time interval between measurements was set to be 30 min up to 24 h.

Table 1
Characteristics of polymers used in this study.

Polymer	M _n ^a	PDI ^b	T _g ^c /K
PMEA	26k	3.23	240
PMMA	85k	1.09	401
dPMMA	93k	1.07	403

^a M_n; The number-average molecular weight determined by GPC calibrated using PMMA standards.

^b PDI; Polydispersity index determined by GPC.

^c T_g; The bulk glass-transition temperature determined by DSC.

2.5. Neutron reflectivity (NR) measurements

The density profile of the blend films along the depth direction was examined by NR with a SOFIA reflectometer at the Materials and Life Science Experimental Facility, Japan Proton Accelerator Research Complex (J-PARC) [27,28]. A Teflon-made reservoir filled with D₂O was mounted onto the film. The measurements were conducted in air, and then, in D₂O after pre-immersion for 24 h at room temperature, which enables the film structure to reach a quasi-equilibrium state. A beam of neutrons with a wavelength (λ) that ranged from 0.25 to 0.88 nm at a resolution of 3% was guided into the specimen from the quartz side. Details of our experimental setup are described elsewhere [29,30]. The reflectivity was calculated on the basis of the model (b/V) profile along the depth direction by means of Parratt32 software, a freeware program from the Hahn-Meitner Institute (HMI). The (b/V) values of PMEA, PMMA, dPMMA, SiO₂, and D₂O used for the calculation were 1.15×10^{-4} , 1.04×10^{-4} , 7.02×10^{-4} , 3.48×10^{-4} , and $6.38 \times 10^{-4} \text{ nm}^{-2}$, respectively.

2.6. Sum-frequency generation (SFG) spectroscopy

The aggregation states of polymers and water at the interface were examined by SFG measurements [31–35]. SFG spectra were collected with visible light with a λ of 532 nm and tunable infrared (IR) beams traveling through the prism and overlapping at the interface between film and air or H₂O. The measurements were carried out at room temperature using one type of polarization combination, namely *ssp* (SF output, visible input, and infrared input). Details of our experimental setup are described elsewhere [34].

2.7. Platelet adhesion tests

Blood was drawn from healthy volunteers and mixed with sodium citrate. The platelet-rich plasma was then obtained by centrifugation [20,21]. The platelet concentration was determined by an automated hematology analyzer. Before the tests, the films were immersed in water for a predetermined time. Then, the platelet suspension was placed on each film surface at room temperature for 1 h. After washing the platelets with phosphate buffered saline (PBS), the adhered platelets were fixed by immersing the films in glutaraldehyde in PBS. Samples were freeze-dried prior to scanning electron microscopy.

3. Results and discussion

Panels (a, b) of Fig. 1 show AFM height and phase images, respectively, of the PMEA/PMMA (10/90) blend film immersed in water for 24 h. Both images were featureless, meaning that the blend film was miscible and structurally stable without any collapse from conditions like dewetting and dissolution, even in water. Panel (c) of Fig. 1 is a sectional view along the line in panel (a). Solid circles in panel (d) of Fig. 1 show a root-mean-square surface roughness (R_{rms}) for the blend film as a function of immersion time in water. The R_{rms} values were approximately 0.31 nm and remained unchanged for 24 h, indicating that the flatness of the blend film at the outermost region could be kept at the nanometer-level, even in water.

While the interfacial roughening of the blend film did not occur in water, the bubble contact angle (θ) on the blend film measured in water clearly changed with increasing immersion time, as shown by open circles in Fig. 1(d). The initial θ value of $127.5 \pm 0.7^\circ$ right after water immersion slightly increased to $130.6 \pm 0.2^\circ$ after 12 h, meaning that the structural reorganization of the blend, or PMEA,

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