Stability of adhesive interfaces by stereocomplex formation of polylactides and hybridization with nanoparticles

Shinya Fujishiro [a], Kai Kan [a, b], Mitsuru Akashi [c], Hiroharu Ajiro [a, b, d, *]

[a] Graduate School of Materials Science, Nara Institute of Science and Technology, 8916-5, Takayama, Ikoma, Nara 630-0192, Japan
[b] Institute for Research Initiatives, Nara Institute of Science and Technology, 8916-5, Takayama, Ikoma, Nara 630-0192, Japan
[c] Graduate School of Frontier Biosciences, Osaka University, 2-1 Yamada-oka, Suita, 565-0871, Japan
[d] JST PRESTO, 4-1-8 Honcho, Kawaguchi, Saitama, 332-0012, Japan

ABSTRACT

In the creation of controllable selective adhesive materials, we have utilized a stereocomplex (SC) on an adhesive interface. We selected poly(L,L-lactide) (PLLA) and poly(D,D-lactide) (PDLA) initiated benzyl alcohol (PLLAb and PDLAb, respectively) as a substrate and gold nanoparticle-coated PLLA and PDLA (PLLA-Au and PDLA-Au, respectively) as an injection material. Before performing measurements, SC formation was examined via Fourier Transform Infrared Spectroscopy (FT-IR), X-ray diffraction (XRD), and Differential Scanning Calorimetry (DSC). Subsequently, the force acting on the interface after drying additional chloroform between two substrates was measured using lap-shear testing by changing the molecular weight of the PLLA and PDLA adsorbed on gold nanoparticles or the gold nanoparticle concentration. As a result, it was found that optimal conditions exist to show differences. Additionally, until present SC formation has required an organic solvent such as chloroform or acetonitrile. We have discovered that SC formation can be induced using novel organic solvents approved by the Food and Drug Administration (FDA). We anticipate applications for this study in the creation of biodegradable medical adhesive materials where these materials can be released based on environmental considerations using the selective adhesion behavior and induce SC formation through the use of novel solvents.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Bio-based polymers have received considerable attention in research over recent decades because of the development of alternative polymer materials based on oil resources for environmental problems [1–3]. In particular, polylactide (PLA) is representative of a bio-based polymer as a biomass. PLA possesses biocompatible and bioabsorbable properties, and has been widely applied for artificial bones [4,5], sutures [6], disposable packages [7], films [8,9], and textiles [10]. However, its thermal properties and mechanical strength limit its range of applications.

One of the approaches to solve these issues is the utilization of stereocomplex (SC) formation. Poly(L,L-lactide) (PLLA) and poly(D,D-lactide) (PDLA) are enantiomers of each other, and they form a racemic crystal when mixed together through weak polymer-polymer interactions, resulting in improved melting points compared to homo crystals [11–13]. SC has been employed for various material preparations, such as hydrogels [14–16], nanoparticles [17], and injectable gels [18]. Our group has also reported on various PLA materials, such as those created by rapid layer-by-layer SC formation by inkjet systems [19,20], simultaneously improving the melting point and thermodegradation temperature by modifying both ends of the SC [21], anti-bacterial SC by catechin introduction at the initiating moiety [22], and dynamic nanostructural control by imine-amine transformation using vanillin [23]. More recently, we investigated the weak interactions between two separated surfaces coated with PLLA and PDLA, using a surface force apparatus (SFA) that can measure a weak force with high sensitivity [24]. It was in light of the utilization of SC using two separate surfaces to achieve selective adhesion. However, the results were observed over a small area and the concept was not based on the application of polymer materials. In order to develop a practical system for material usage, further control of selective adhesion at the cm order at least is desirable, together with the possible additional function at the surface. Tsujii and coworkers

have reported the interaction between two surfaces of condensed polymer brushes [25]. Takahara and coworkers have also reported the polyelectrolyte interaction between two surfaces [26]. Similarly, layer-by-layer assembled films were also created by Serizawa and coworkers [27].

Selective SC formation using PLLA and PDLA was investigated using the adsorption of enantiomeric PLA on a gold surface grafted with PLLA [28], silsesquioxane [29], and block copolymers [30]. In our previous work that estimated SC formation of PLLA and PDLA on facing substrates [24], the polymer length was estimated to be about 80 nm in the case of PLA (M_n = 2000); selective adhesion between heterogeneous and homogeneous surfaces was achieved with PLLA and PDLA. This results could be due to the higher crystallization rate and stability of the SC crystal than those of alpha-form, as evidenced by their melting points [11]. Therefore, this study is motivated to investigate the use nanoparticles inserted into the interface between the PLLA substrate and the PDLA substrate.

The development of nanotechnology has enabled the easy control of nano-ordered particles, such as silica gel [31], polystyrene [32], silver [33], and cadmium [34]. These particles have been utilized for research on biomedical applications. The nanoparticles are of interest because of their size: particles of the nanometer order exhibit extraordinary electrical, magnetic and optical properties. In other words, localized surface plasmon resonance (LSPR) and quantum dots (QD) of nonlinear optical phenomena expressed by metal nanoparticles possess optical properties that depend on particle size. For example, metal nanoparticles are different from the metal clusters of gold [35] and silver emitted by LSPR in the bulk state, exhibiting colors such as red, blue and yellow. Thus, due to the color of the metal nanoparticles, application as imaging materials without fading (as long as they maintain form) can be expected. Furthermore, hybridization with inorganic compounds and interacting polymers produce useful materials [36]. This phenomenon makes it possible to modify the properties of nanofilms as adhesive moieties between two substrates with PLLA and PDLA by hybridization.

In this study, using the in-between PLA stereocomplex two substrates, the objective is to develop selective adhesive systems where the adhesive force acting on the adhesive interface can be controlled by adding stereocomplex forming solvent, especially chloroform, and nanoparticles modified with PLA. Firstly, we prepared gold nanoparticles coated with PLA in order to control the force acting on the adhesive interface. Then, we prepared two sheets of PLA films on each polypropylene (PP) substrate. The PLA-coated gold nanoparticles and chloroform were injected between the PLA films on PP substrates, and the films were subjected to lap-shear testing after contacting two surfaces with glass plates as substrates by crimping. Furthermore, we measured the gold nanoparticle concentration and the various forces acting on the adhesive interface by changing the PLA molecular weight and compared the results between the substrates. To the best of our knowledge, this is the first study utilizing SC-PLA and nanoparticles between two substrates for adhesion.

2. Experimental

2.1. Materials

The commercially available monomers, (L,L)-lactide and (D,D)-lactides (Musashino Chemical Laboratory, Ltd., Japan, Tokyo) were recrystallized from hexane/ethyl acetate (8/2, v/v) for purification. The polymerization catalyst, tin (II) ethylhexanoate (Sn(Oct)$_2$) was purchased and used without further purification (Tokyo Chemical Industry, Japan, Tokyo). Bulk polymerization of lactides was achieved as reported elsewhere [37]. HAuCl$_4$·4H$_2$O (99%, Wako, Japan),

N(C$_8$H$_{17}$)$_4$Br (Wako, Japan), NaBH$_4$ (95%, Wako, Japan), and C$_{11}$H$_{23}$SH (Wako, Japan) were used as received. Benzyl alcohol-terminated PLAs defined as PLLAb (M_n = 8.5 × 10^3) and PDLAb (M_n = 8.3 × 10^3), were prepared according to previously reported procedures (Supporting Information, Scheme S1) [21].

2.2. Measurements

Size-exclusion chromatography (SEC) was carried out using a Chem NAV system with polystyrene standards at 40 °C, equipped with PU-2080, AS-2055, CO-2065, and RI-2031 (JASCO Corporation, Japan). Two commercial columns (TSKgel SuperH4000 and TSKgel GMHXL, Tosoh Corporation, Japan) were connected in series, and tetrahydrofuran (THF) was used as the eluent. Proton nuclear magnetic resonance (^{1}H NMR) spectra were measured by JEOL JNM-ECX 400 (400 MHz) in deuterated chloroform to which tetramethylsilane was added as an internal reference. FT-IR/ATR spectra were obtained with a Spectrum 100 FT-IR (IRAffinity-1S ATR, Shimadzu Corporation, Japan). The interferogram was co-added eight times and Fourier-transformed at a resolution of 4 cm^{-1}. X-ray diffraction (XRD) patterns were obtained with a Rigaku RINT-TTR III/NM (Rigaku Corporation, Japan). Cu Kα (λ = 0.154 nm) was used as the X-ray source, and the instrument was operated at 50 kV and 300 mA with a Ni filter (Rigaku ultra ×18). The samples were examined at 2θ = 5°¬35° at a scan rate of 0.5°/min. Differential scanning calorimetry (DSC) was performed with DSC-60 Plus and TAC/L systems (Shimadzu Corporation, Japan) under a nitrogen atmosphere. The heating and cooling rates were 10°C/min, and the second heating was monitored. Thermogravimetric analysis (TGA) was performed with a TGA-50 (Shimadzu Corporation, Japan) under a nitrogen atmosphere. The heating rate was 10°C/min. Dynamic light scattering (DLS) measurements were carried out with a Malvern ZEN 3600 Zerasizer NANO-ZS (He Ne laser, 633 nm) until a PLA concentration of 1.0 mg/mL was reached. The intensity of scattered light was measured at 173° and the refractive indices of chloroform, acetonitrile, dimethyl carbonate, dimethyl succinate, dimethyl glutarate, dimethyl adipate and dimethyl maleate were set at 1.44, 1.34, 1.37, 1.42, 1.42, 1.43, and 1.44, respectively. These samples were filtered through a 0.2 μm filter (Toyo Roshi Kaisha, Ltd., Japan) before use. Transmission electron micrographs (TEM) were recorded with a JEM-2200FS, JEOL (200 kV). The PLA-Au was dissolved in chloroform (1 mg/mL), and the suspension solutions were dropped on a copper grid (200 mesh) coated with a holey carbon. The grid was dried in desiccator under N$_2$ atmosphere. Ultraviolet-visible (UV-vis) absorption spectroscopy were analyzed with UV-2600 (Shimadzu Cooperation, Japan). The samples were dissolved in chloroform at required concentration for measurements.

2.3. Preparation of gold nanoparticles stabilized by C$_{11}$H$_{23}$SH and tiol terminated PLA

PLA end capped by a protected thiol (PLA-SH; Supporting Information, Scheme S2) [38], and gold nanoparticles were prepared according to the literature [39,40]. The typical procedure is as follows.

In a round-bottom flask, 26.8 mg of HAuCl$_4$-4H$_2$O was dissolved in 2.7 mL of deionized water. Into the aqueous solution, 0.1 M of a N(C$_8$H$_{17}$)$_4$Br solution (N(C$_8$H$_{17}$)$_4$Br/Au = 2.22/1, mol/mol) in CHCl$_3$ was slowly added under rapid stirring. After the AuCl$_4$ was confirmed to be completely transferred to the organic phase, 0.01 M of a PLA-SH solution (-SH/Au = 1/3.5, mol/mol) in CHCl$_3$ was added to the organic solution. Then, 0.41 M of a freshly prepared aqueous solution of NaBH$_4$ (NaBH$_4$/Au = 11.0/1, mol/mol) was slowly added, and rapidly stirred for 4 h. The organic phase was