Title	未利用芳香族アミノ酸 4-アミノ桂皮酸を用いた芳香族バイオベースポリマーの開発
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Development of aromatic bio-based polymers derived from unused aromatic amino acid, 4-aminophenylalanine

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Background

Development of high-performance bioplastics, which are indispensable to establish green sustainable low-carbon based society, poses a challenge to the scientific society worldwide as commonly developed aliphatic bio-based polymers such as poly(lactic acid)[1], polyhydroxyalkanoate[2], poly(butylene succinate)[3], and polyamides[4] have low thermomechanical performance, and hence, limited industrial applications. A number of aromatic biopolyamides (PA)s[5] and biopolyimides (PI)s[6] from the photodimer of microorganism-derived 4-aminocinnamic acid (4ACA) which was biosynthesized based on shikimic pathway[7] have been developed. Isolated from the same pathway, another functionalized aromatic amino acid, 4-aminophenylalanine (4-APhe), as diamine monomer, is also promising for developing high-performance polymers.

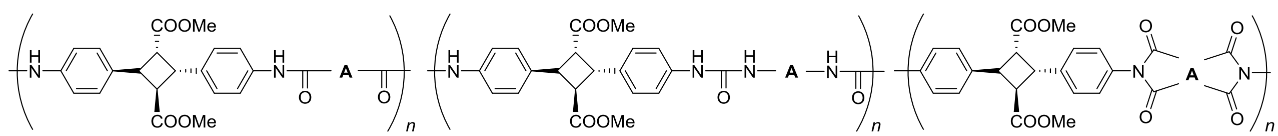

Figure 1: Bio-based high-performance polymers derived from 4-aminocinnamic acid.

Aim

The primary purpose of the present study is to investigate the possibilities of synthesizing a large number of unconventional, alternative unreported high-performance polymers (specifically, polyureas and polyimides) from a bio-based source. My research goals also include investigation of: (1) thermal properties, (2) mechanical properties, and (3) some of the practical applications of the synthesized polymers. Here, I have synthesized new bio-based polyureas (PUs) and polyimides (PIs) using 4-aminophenylalanine (4-APhe) as a diamine monomer bioavailable by fermentation process using genetically modified *Escherichia coli*. The polyureas (PUs) and polyimides (PIs) were synthesized by carrying out chemical reactions using 4-APhe with a series of diisocyanates and dianhydrides respectively. High solubility of the polymers keeping aromatic structure is expected because of the flexible moiety of aliphatics in the polymer backbone and asymmetric structure. The introduction of aromatic rings in the backbone of polymer chain boosts their thermal and mechanical performances and widens their application fields into electronics, automobiles, and optical materials.

Experimental

Instrumentation. The data for this research were gathered using latest sophisticated techniques at JAIST such as Nuclear magnetic resonance (NMR) measurements by Bruker biospin AG 400 MHz; Fourier-transformed infrared (FT-IR) spectra were recorded with a Perkin-Elmer Spectrum One spectrometer; mass spectra were measured using a Fourier-transformed ion cyclotron resonance mass spectrometer (FT-ICR MS, Solarix); X-ray diffraction (XRD) using rotor X-ray emitter

(RINT 2000; Rigaku Smart Lab); tensile measurements were carried out on a tensiometer (Instron 3365, Kawasaki, Japan); number average molecular weight (*M*n), weight average molecular weight (*M*w) and molecular weight distribution (PDI) of the polymers were determined by gel permeation chromatography (GPC; Shodex GPC-101 with a tandem connection column system of KD-803 and KD-807 (Shodex, Tokyo, Japan)); ultraviolet-visible (UV-vis) transmission spectra were recorded by Perkin Elmer, Lambda 25 UV/Vis spectrometer, Differential scanning calorimetry (DSC) was carried out by using Seiko Instruments SII, X-DSC7000T, thermal analysis by thermogravimetry (TGA; SSC/5200 SII Seiko Instruments Inc.).

Materials. The materials used in the research are of super grade quality and from renowned chemical companies like Aldrich, TCI, Japan, Kanto, Japan, Watanabe chemicals, Japan. The selection of appropriate monomers is necessary for tuning the properties of polymers. Aromatic diisocyanates were selectively and preferably chosen for the synthesis of polyureas as the aromatic diisocyanates such as diphenylmethane diisocyanate (MDI) or toluene diisocyanate (TDI) are more reactive than the aliphatic ones such as hexamethylene diisocyanate (HDI) or isophorone diisocyanate (IPDI). The compatibility factor with aromatic diamine in aromatic diisocyanates also plays pivotal role in their selection besides the economic factor. TDI and MDI are generally less expensive and more reactive than other isocyanates. The influence of the structure of the aromatic diisocyanates on the preparation and the properties of polyureas were also investigated through this research. Dianhydrides for the synthesis of polyimides are also carefully chosen. Dianhydrides such as pyromellitic dianhydride (PMDA: from TCI), 1,2,3,4-tetracarboxycyclobutane dianhydride (CBDA: from Aldrich), 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA: from Aldrich), 4,4'-oxidiphthalic anhydride (OPDA: from Aldrich), 3,4,3',4'-biphenyltetracarboxylic dianhydride (BPDA: from Aldrich), and 3,3',4,4'-diphenylsulfone tetracarboxylic dianhydride (DSDA: from Aldrich) were purified by using sublimation process or recrystallized in acetic anhydride by refluxing for 5h and then cooling to 0~5 °C. The crystals were carefully collected by filtration, washed in hot dioxane, and dried in *vacuo*. The solvents used in the chemical reactions were either purified by distillation or used as such if super grade quality.

Results and discussion

In chapter 2, syntheses, characterization, thermal and mechanical properties of a series of aromatic polyureas (PUs) from 4-aminophenylalanine (4-APhe) are described. Most of PUs are processable into films or fibers having excellent mechanical properties; mechanical strength at maximum around 150 MPa and strain energy density around 10 J/cm^3 at maximum, which means that PUs are much tougher than those of conventional bioplastics. The synthesized PUs are also soluble in some of the commonly used organic solvents like DMSO, DMF, DMAc, NMP which make their processability easier.

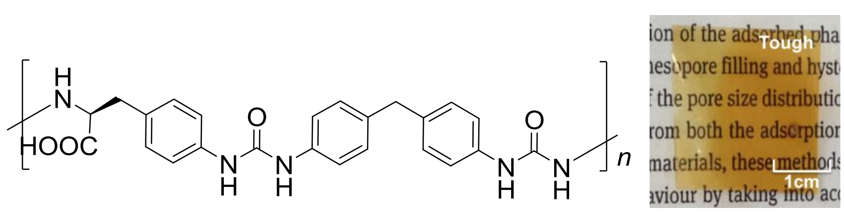

Figure2: Representative chemical structure and film image of PU.

Later, the cell adhesion was also checked onto different polyurea films in order to check the cell-compatibilty. It was found that PU films showed good cell compatibility. A mouse fibroblast-like cell line (L929) was selected for all the biological assays in order to determine compatibility factor.

Chapter 3 discusses about further attempts or possibilities to use 4-aminophenylalanine as aromatic diamine monomer for the synthesis of bio-poly(amic acid) (BPAA) or bio-polyimide (BPI). The project was designed to improve the thermo-mechanical properties of polymeric substances synthesized from 4-APhe. Polyimides show improved thermo-mechanical properties based on the stiff aromatic backbones resulting from both dianhyrides and diamines constituents. 4-APhe reacted with various dianhydrides to create poly(amic acid), and then successive heat treatments yielded the polyimides (PI). The combination of 3,3’,4,4’-benzophenone tetracarboxylic dianhydride (BTDA), 4,4’-oxidiphthalic anhydride (OPDA), 3,4,3’,4’-biphenyltetracarboxylic dianhydride (BPDA) with 4-APhe (diamine) created the toughest films than other dianhydrides with 4-APhe. The PAA films were unbreakable when folded completely. Over most of the conventional plastics, PIs show high thermal and mechanical performance: a 10 % weight loss temperature (T_{10}) over 427 °C, a glass transition temperature (T_g) over 350 °C, high tensile strength and a high Young’s modulus, with maximum values of 75 MPa and 5 GPa, respectively, and good cell compatibility. The properties of PI films such as high mechanical strength and good transparency make them useful candidates in the development of electronic devices.

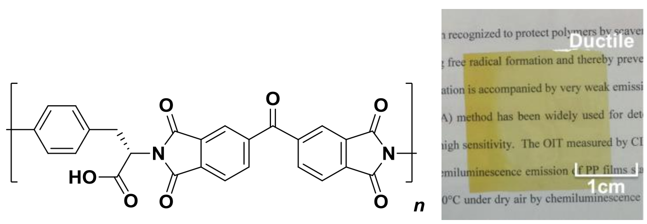

Figure3: Representative chemical structure and film image of PI.

Later in chapter 4, the composites materials using carbon fibres and the matrix of synthesized polymers (polyureas and polyimides) were developed by stacking alternatively the layers of carbon fibres and polymer. The mechanical strength of the composites was tested.

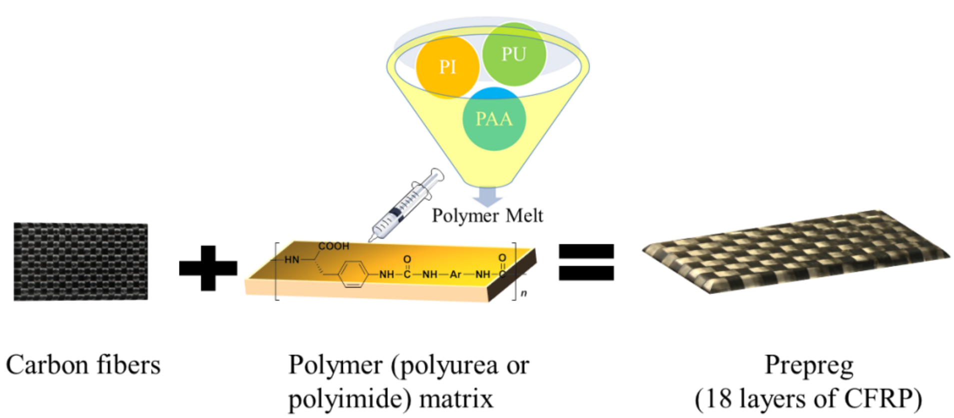

Figure4: Representative cartoon illustration of preparation of polymer composites.

The results showed the composites have good mechanical strength compared to the carbon fibres or polymer considered separately because of the reinforcement effects. Such composites materials developed with sophisticated techniques could potentially be used in various practical applications such as automobiles, fishing nets etc.

On the basis of the results of this research about development of unconventional alternative novel bio-based polymers, specifically, polyureas and polyimides, it was concluded that bio-polymers prepared showed molecular weights high enough to evaluate the thermal and mechanical properties. The polymer films showed excellent cell-compatibility which makes them a potential candidate in ophthalmological applications. Some of the polymeric films created were so flexible and tough that they were unbreakable when folded completely. Further challenges lie in improving the transparency of PU films, ductility of the PIs, incorporation of metal ions in polymeric materials to investigate further improvement or discovering new properties, preparation of nano-composites using these polymeric materials, biocompatibility and processibilties of the polymers so as to widen their usage in industrial applications or practical devices to make life easy for human comfort.

KEYWORDS. Amino acids; Polyureas; Poly(amic acid)s; Polyimides; Mechanics; Bioplastics; Polymer films, High-performance polymers

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Chapter 4: Development of carbon fibre reinforced polymers (CFRP) using synthesized biopolymers in the present research and investigation of their mechanical properties.
Chapter 5: Conclusive remarks and future potential of this research
Achievements
Acknowledgements

Publications

1. **Manjit Singh Grewal**, Kazuya Taya, Seiji Tateyama, Tatsuo Kaneko*, *Preparation of tough biopolyurea films from aromatic amino acid as diamine monomer*, *Macromolecular symposia*, accepted for publication on 7 February 2017.
2. **Manjit Singh Grewal**, Kazuya Taya, Seiji Tateyama, Tatsuo Kaneko*, *High performance bio-polyimides from 4-aminophenylalanine, an exotic aromatic amino acid*, (script in preparation).