Abstract

The research in this thesis focused on the synthesis of high performance polyamides derivatives from bio-based 4-aminocinnamic acid. The The development of these high performance bio-based polymers was crucial to establish sustainable low-carbon society. The important and interesting results throughout this study are summarized in the following parts.

In Chapter 2, bio-based aromatic diamine 4,4′-diamino-α-truxillic acid was successfully prepared as a photodimer of 4-aminocinnamic acid, bioavailable from genetically-manipulated *Escherichia coli*, even though the direct biosynthesis of aromatic diamines have never been reported. Photo-irradiation was a good synthesis method because it can be accurately targeted and highly selective. The single crystal of 4,4'-diamino-α-truxillic acid dihydrochloride was used to confirm the *trans*-stereoisomer product after UV irradiation. It also indicated that 4, 4'-diamino-α-truxillic acid dihydrochloride and 4,4'-diamino- α-truxillic acid methyl ester had high purity because small needles of crystal were able to be prepared. The polyamides was prepared from 4, 4'-diamino-α-truxillic acid methyl ester and phthalate acids, both bioavailable compounds. The relationship of its molecular structure and properties was clarified. The polyamide showed high thermal stability and high T_g. Nevertheless, their hydrolyzability were the crucial problems when used as high performance polymer in manufacturing process.

Chapter 3 described the synthesis of high performance bio-based PU which were used in place of the polyamide. The synthesis of PUs was classify and quick. The reaction time only needed 2 hours at 100^{o}C. The PUs showed high molecular weight and good thermal properties. In case fo PUs, they showed ultra high thermal resistance of T_g over 300^{o}C and the solubility of PUs showed improvement because polyureas can dissolve in DMF/water mixed solvent. Based on the carboxylic acid I have successfully modified polymer under the film formed by the metal cation. I confirmed the mechanism of the modified film by FT-IR and research the modified film from thermal, mechanical and optical properties.

Not only thermal and mechanical properties, but also degradations of PUs were studied in Chapter 4. Because there are fuctional group, cyclobutane, existed, it became possible that the degradation products completely broke into small molecules. For the degradation, the photolysis speed was fast, only 28-32hs and hydrolysis speed was slow, 7 days, and the products include the diamino which could be the renewable compound for methyl diphenyl isocyanate and from the photolysis the products also had the cinnamon compound.

In summary (Chapter 5), the development of aromatic polyureas not only showed good performance on the thermal and mechanical properties but also showed excellent degradation process by UV and hydrolysis. On one hand the polyureas' thermal property just was a little weaker than polyamides, on the other hand the mechanical property was stronger than the polyamides. The degradation products of the polyureas could be the renewable sources for the polymers, which was useful to establish sustainable green society. They could be used to reduce the serious problems of plastic waste and petroleum source.

Keyword: bioplastics, polyamide, polyurea, reinforcement, degradation