

Application of cyclodextrins in thermosetting polymers: cyclodextrin-polyhemiaminal composite polymers and inclusion complex formation of [aromatic diamines@cyclodextrin]

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(課程博士・様式7) (Doctoral qualification by coursework, Form 7)

学位論文要旨

Abstract of Doctoral Thesis

Course : Optoelectronics and Nanostructure Science

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Title of Thesis : Application of cyclodextrins in thermosetting polymers: cyclodextrin-polyhemiaminal composite polymers and inclusion complex formation of [aromatic diamines@cyclodextrin]

(熱硬化性ポリマーにおけるシクロデキストリンの応用：ポリヘミアミナル架橋ポリマーと[芳香族ジアミン@cyclodextrin]包接錯体)

Abstract : Typical thermosetting polymers containing high cross-link density are difficult to recycle, reprocess, and solubilize in organic solvents causing serious environmental and waste management problems. The most reliable method is to incorporate dynamic bonds either in a cross-linked knot or in the monomer to improve solubility, thermal stability, and recyclability. Polyhemiaminal (PHA) cross-linked polymer is a new class of thermosetting polymers prepared by polycondensation of diamine and formaldehyde at 50 °C and subsequently cyclized to form polyhexahydrotriazine (PHT) by the removal of water at a high temperature. Thus, PHT polymers prepared are found to exhibit high mechanical strength (Young's moduli ~14 GPa when 4,4'-oxydianiline (ODA) is used as a monomer) and chemical recycling at pH < 2. Numerous PHA thermosetting polymers have been designed for automotive, aerospace, and adhesive coating applications. However, low thermal stability is one of the issues of PHA polymers, which is due to thermally labile PHT knots. Herein, I synthesize composite PHA polymers by reacting formaldehyde with sonicated precursor solution of ODA and cyclodextrins (α -, β -, and γ -) (CDs), demonstrating that the material obtained under optimal conditions (ODA: CD molar ratio of 1:0.5, saturated (37%) aqueous formaldehyde solution) exhibits good film formability and high thermal stability. Two characteristic decomposition

temperatures are observed in TGA, such as the early-stage decomposition of CDs and the final polymer decomposition to furnish residual char. Early-stage decomposition of CDs renders the high thermal stability of PHA polymers. Notably, CDs/PHA composites are processed in a solution containing *N*-methyl-2-pyrrolidinone containing 8–9 wt% LiBr at 80 °C to recover the PHA matrix. Various spectroscopic techniques confirm CDs-based polymers and hemiaminal core formation, and the chemical recyclability of polymers is checked by pH resolution.

In another project, I studied the inclusion complexes (ICs) formation between β -CD (host) and some aromatic diamines (guests) by mixing in hot water, co-precipitation, and solid-state grinding methods. Aromatic diamines are widely used to prepare nitrogen-based thermosetting polymers such as polyimide, polyamide, and polyurea intended for automotive, aerospace, and adhesive coating materials. Recent attention has been growing on CDs-bearing thermosetting polymer to improve solubility in solvents as well as to improve thermal stability. Generally, the synthesis of CDs-bearing polymers is performed by including CDs into aromatic diamines followed by a polycondensation reaction. Various methods used to prepare ICs are co-precipitation, freeze-drying, and solid-state grinding. The co-precipitation method is typically used to prepare CD-ICs of aromatic diamines and other aromatic guests using a co-solvent. Co-solvent is used to dissolve guest molecules and diffuse into an aqueous CD solution to precipitate ICs. As CDs have a large hydroxyl surface, guest dissolution in alcohol is unnecessary, and the simple dissolution of CDs and aromatic guests in hot water could form ICs. In this process, ICs formation is carried out by mixing aromatic diamine into the aqueous β -CD solution at 80 °C for 24 h while high-speed stirring magnetically. Also, the solid-state grinding method is used to prepare ICs of studied diamines and β -CD by adding a small amount of water (to make a slurry) to favor the inclusion process. Thus, ICs formed by mixing in hot water and solid-state grinding are crystallized by changing the saturation rate and then cooling at 4 °C. The structure of the ICs is confirmed by chemical shift changes of cavity protons of β -CD and the correlation between aromatic protons of diamines and β -CD in ^1H - ^1H ROESY NMR in D_2O . The stoichiometric ratio of ICs is determined by Job's plot and ^1H NMR titration methods in solution.