

論文 / 著書情報
Article / Book Information

題目(和文)	不飽和ポリヒドロキシアルカン酸の合成と化学修飾
Title(English)	Synthesis and Chemical Modification of Unsaturated Polyhydroxyalkanoates
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出典(和文)	学位:博士(工学), 学位授与機関:東京工業大学, 報告番号:甲第11188号, 授与年月日:2019年3月26日, 学位の種別:課程博士, 審査員:柘植 丈治,北本 仁孝,福居 俊昭,和田 裕之,林 智広,阿部 英喜
Citation(English)	Degree:Doctor (Engineering), Conferring organization: Tokyo Institute of Technology, Report number:甲第11188号, Conferred date:2019/3/26, Degree Type:Course doctor, Examiner:,,,,,
学位種別(和文)	博士論文
Category(English)	Doctoral Thesis
種別(和文)	論文要旨
Type(English)	Summary

論文要旨

THESIS SUMMARY

系・コース： Department of, Graduate major in	材料 ライフエンジニアリング	系 コース	申請学位 (専攻分野) : Academic Degree Requested	博士 Doctor of	(工学)
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要旨 (英文 800 語程度)

Thesis Summary (approx.800 English Words)

Polyhydroxyalkanoates (PHAs) are a kind of the bio-polyester and used as a biodegradable plastic. Despite their high potential for medical applications, the drawbacks existed in PHA also limit the application scope of PHA as a biomedical and biodegradable polymer. There are two major drawbacks, one is the mechanical properties, PHAs are classified into three main classes, short-chain-length (scl) PHA, medium-chain-length (mcl) PHA and long-chain-length PHA according to the carbon chain length of the monomers. Due to the effect of carbon chain length, scl-PHAs are too rigid and brittle, and these shortcomings should be improved for biomedical applications. In contrast, despite mcl-PHAs and lcl-PHAs are elastomeric, the low mechanical strength limits the application of these PHAs in the medical field. Another drawback is low hydrophilicity. In this study, in order to prepare the PHAs which are more suit for biomedical materials field, the PHA containing unsaturated bond were produced by biosynthesis or chemical synthesis methods, after it, here focused on a thiol-ene click reaction as a tool to alter the hydrophilicity and mechanical properties of PHA containing unsaturated bond via side-chain modification of double bond.

In Chapter 1, I presented the general introduction of petroleum-based plastics material, waste petroleum plastics issue, biodegradable plastics, structure and physical properties of PHAs, modification of PHAs, and unsaturated PHAs.

In Chapter 2, the biosynthesis of unsaturated PHAs by several type strains of *Pseudomonas* (*P. putida*, *P. citronellolis*, *P. oleovorans*, and *P. pseudoalcaligenes*) and a typical PHA producer, *P. putida* KT2440, using gluconate, dodecanoic acid, and oleic acid as the sole or mixed carbon source were investigated. As a result, two unsaturated PHA monomers (3H5DD and 3H5TD) were identified. However, only two type strains of *P. putida* and *P. citronellolis* have the ability to produce unsaturated PHAs in this study. When oleic acid was used as the carbon source, the largest 3H5TD content of 12 mol% was obtained from *P. citronellolis*, and it further increased to 16 mol% when the mixture of gluconate and oleic acid was used. Based on the observations, biosynthetic pathway of unsaturated PHA monomers was discussed. Moreover, a hydrophilicity mcl-PHA was synthesized by the thiol-ene click reaction between unsaturated PHAs and 3-mercapto-1-propanol. The water contact angle of mcl-PHAs decreased by 10° after modification. It would be more suited materials for medical application than untreated PHAs.

In Chapter 3, the chemical synthesis of unsaturated PHA was presented. The methylenation reaction of poly(3-hydroxybutyrate) [P(3HB)] and mcl-PHA carbonyl group using the dimethyl titanocene (Petasis reagent) were carried out. Various reaction conditions, such as reaction temperature, the ratio of Petasis reagent in the reaction system, and reaction time, were investigated. Four different linkage structures [P(3HB) backbone structure, P(3HB) terminal structure, methylenation P(3HB) backbone structure, and methylenation P(3HB) terminal structure] were detected in the reaction products of P(3HB), the highest methylenation conversion rate was 12.3%. Furthermore, the hydrophilized P(3HB) was synthesized by the thiol-ene click reaction between methylenation P(3HB) and 3-mercapto-1-propanol. The water contact angle of P(3HB) homopolymer was $88.5 \pm 2.5^\circ$, which decreased to $67.1 \pm 0.9^\circ$ for the UV treated methylenation P(3HB).

In Chapter 4, a possibility of thiol-ene click chemical reaction between unsaturated mcl-PHAs and poly(3HB-co-3-mercaptopropionate) [P(3HB-co-3MP)] was studied. P(3HB-co-3MP) is a kind of biopolyester containing sulfur backbone. The mechanical properties of P(3HB-co-3MP) is similar to P(3HB) homopolymer and also has high crystalline. There is great complementarity of physical properties between unsaturated mcl-PHAs and P(3HB-co-3MP). The blends of P(3HB-co-37 mol% 3MP) and unsaturated mcl-PHAs were prepared by hot-press, and a relatively transparent blend film was obtained when the mass content of mcl-PHAs was above 30 wt%. Unfortunately, according to the results of ^1H NMR analysis, the evidence of reaction between unsaturated mcl-PHAs and P(3HB-co-3MP) was not found. To confirm the terminal thiol group is formed during the heating process in P(3HB-co-3MP) copolymer, the thermal behavior and degradation of P(3HB-co-3MP) copolymer were investigated. The results showed P(3HB-co-3MP) has higher heat-resisting stability than P(3HB) homopolymer, and difficult to form terminal thiol group under given heating conditions.

In Chapter 5, the results and conclusions of this study were summarized.

On the basis of the results mentioned above, this study provides some basic knowledge on PHAs containing unsaturated bond produced by bio-synthesis and chemical synthesis methods. The results of unsaturated PHA monomers biosynthesized by various *Pseudomonas* strains offer some basic references for *Pseudomonas*-relating research and imply that *Pseudomonas* strains have a high ability to product unsaturated PHA monomer. The methylenation reaction with Petasis reagent is a way to introduce unsaturated bond into PHAs. Because the modification of saturated structure is hard to achieve, especially it has meaning for saturated PHAs. To further improve the physical properties of PHAs by post-biosynthesis method, it needs to confirm the possibility of some thiol-ene click reactions occurred with unsaturated PHAs. I believe this study serves as a basic platform for future studies of tunable PHA materials thorough modification of unsaturated bond. The modified PHAs would be more hydrophilic and have excellent mechanical properties. They are suitable materials for biomedical field and could be used as bio-active molecules or tissue scaffold in tissue engineering.

備考：論文要旨は、和文 2000 字と英文 300 語を 1 部ずつ提出するか、もしくは英文 800 語を 1 部提出してください。

Note: Thesis Summary should be submitted in either a copy of 2000 Japanese Characters and 300 Words (English) or 1 copy of 800 Words (English).

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