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論 文 要 旨

THESIS SUMMARY

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要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

The environmental impact of conventional plastics, particularly their contribution to marine pollution, necessitates the development of bio-based, biodegradable materials capable of degrading effectively in various natural environments. Among such materials, polyhydroxyalkanoates (PHAs) have emerged as promising candidates due to their biodegradability and bio-based nature. However, controlling the biodegradation rate of PHAs is critical for meeting specific functional requirements in practical applications. This study explores the biodegradability of PHAs, evaluates various synthetic and microbial polyesters as base polymers, and investigates strategies to modify their structures for tailored biodegradation rates.

In Chapter 2, the biodegradability of synthetic and bacterial polyesters was examined in seawater from Suruga Bay, Shizuoka Prefecture, Japan, through weight loss measurements, surface morphology analysis, and microbial population studies. Biochemical Oxygen Demand (BOD) tests were also performed to assess biodegradability. The results showed that 3-hydroxybutyrate (3HB)-based polymers and polycaprolactone (PCL) were degraded faster than the other biodegradable plastics, notably in deep seawater. Meanwhile, other biodegradable polymers degrade faster in surface seawater. Polylactic acid showed no biodegradability. Surface morphology observations revealed uneven traces and weight reduction on the samples, confirming biodegradation. Microbial analysis suggested differences in microbial activity, indicating environmental variations in species' roles in promoting biodegradation. The findings identified 3HB-based polymers as suitable base materials due to their superior biodegradability and modifiability compared to PCL, which has poor mechanical properties and low melting temperatures.

In Chapter 3, 2-hydroxy-4-methylthiobutyrate (2H4MTB)-containing polymer was biosynthesized using recombinant *Escherichia coli* DH5 α with L-methionine as a precursor. Oxidation treatments using hydrogen peroxide converted sulfide groups to sulfoxide and sulfone, as confirmed by nuclear magnetic resonance (NMR), Fourier transform infrared spectroscopy, and Raman spectroscopy. These modifications increased the films' surface hydrophilicity, as revealed by contact angle measurements. The biodegradation of oxidized and non-oxidized films was compared in seawater from Suruga Bay. Films immersed in deep seawater exhibited greater weight loss, with oxidized films degrading faster than non-oxidized ones. Surface morphology analysis revealed distinct degradation patterns: surface erosion on oxidized films and cavity formation on non-oxidized films. These results highlighted that surface hydrophilicity was not the primary factor influencing biodegradation rates. Instead, changes in polymer crystallinity appeared to play a critical role. BOD tests confirmed that oxidation treatments accelerated biodegradation, demonstrating the feasibility of surface modification as a tool for controlling PHA degradation rates.

In Chapter 4, PHA containing a novel 2-hydroxy-3-(4-hydroxyphenyl)propionate (2H3PhOHP) unit was biosynthesized using L-tyrosine and glucose as precursors. The structure and composition of the polymer were characterized using NMR. After chemical modification of the phenol groups with phosphate compounds, ^{31}P NMR was applied for further confirmation. Material characterization revealed that the polymer exhibited a relatively high glass transition temperature (T_g), attributed to the aromatic groups in its structure. Contact angle measurements showed the hydrophilic nature of the polymer. The biodegradation performance of 2H3PhOHP-containing polymer films was evaluated in seawater. The results demonstrated that the incorporation of the 2H3PhOHP unit significantly reduced the biodegradation rate in deep seawater, likely due to the increased T_g and inhibited crystallization caused by the aromatic groups. These findings suggest that the incorporation of phenolic side groups offers potential for precise control of degradation rates in marine environments.

This study concludes that 3HB-based polymers are promising candidates for biodegradable materials suitable for marine applications. Modifications such as the incorporation of sulfur-containing side chains, surface oxidation, and the introduction of aromatic groups enable control over their biodegradation rates to meet specific application requirements. While tyrosine-derived 3HB-based copolymers offer significant potential for further customization, additional research is required to fully elucidate their degradation behavior and optimize their material properties for broader applications.

These findings provide a foundation for the development of bio-based materials that address the pressing issue of marine plastic pollution, offering environmentally friendly alternatives with tailored performance capabilities.