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PRESS RELEASE

Source: Toyohashi University of Technology, Japan, Committee for Public Relations

Release Title: Terahertz-waves provide a new method to analyze biomass-based plastic
Release Subtitle: Towards the elucidation of the origin of absorption spectra and the development of materials with new functions

Overview

The collaborative research team formed by the Electronics-Inspired Interdisciplinary Research Institute (EIIRIS) and the Department of Applied Chemistry and Life Science of Toyohashi University of Technology and Osaka Institute of Technology employed terahertz-waves, located in the gap between radio-waves and light-waves, as observation probes, and conducted broadband terahertz (THz) spectroscopy analysis on polylactide (PLA) with different polymer crystal structures. As a result, differences in higher-order structure, which are hard to reveal through conventional methods such as X-ray diffraction, were successfully detected with high precision from differences in THz absorption peaks. This achievement suggests that terahertz-waves have the potential to enable the detection of differences in the complex higher-order structures of PLAs and other biomass-based plastics.

The results of this research were published online on Materials Advances of the Royal Society of Chemistry in the June 2 and selected as an Inside Back Cover in the July 21.

[Article URL] https://pubs.rsc.org/en/content/articlelanding/2021/MA/D1MA00195G

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Details

Since polymers (plastics) were first created synthetically, metal, glass, and wooden products have been replaced with plastics and our lives in modern society are supported by a large number of plastic products. At the same time, due to the current problems of marine pollution caused by microplastics and carbon dioxide (CO_2) emitted in the plastic manufacturing process, there is a strong need to use environmentally friendly plastics. Against this backdrop, biomass-based plastic is drawing attention as it is biodegradable and highly carbon-neutral. Basically, polymer properties such as hardness, fragility, workability, and thermal stability are determined not only by the chemical composition but also by the higher-order structure related to the crystallinity, molecular chain length, and chain packing in the solid state. However, unlike widespread petroleum-based plastic, biomass-based plastic does not have a long history and there is little fundamental understanding with respect to its high-order structure and physical properties, which is hindering its spread. In addition, to solve the challenge of how to change the higher-order structure of biomass-based plastic to achieve the desired functions, there is strong demand for the

establishment of nondestructive and noninvasive analysis techniques. The conventional evaluation methods include differential scanning calorimetry (DSC) and X-ray diffraction (XRD); however, DSC involves the destruction of samples and XRD has challenges with its time-consuming measurements, adverse effects on the human body, and the need for analytical expertise.

Under these circumstances, the research team focused on terahertz-waves (1 to 10 THz), located in the gap between radio-waves and light-waves, with a view to using them as a method suited to evaluating polymer structures and physical properties, and moved ahead with the spectroscopy analysis of a wide variety of polymer materials. As a result, the team successfully observed clear THz absorption peaks attributed to the higher-order structure of poly(L-lactide), one type of biomass-based plastic. It is known that changing crystallization temperature results in the formation of PLA with different crystal structures such as α-form (110 ºC) and δ-form (80 ºC). With a focus on this characteristic, the research team carefully prepared samples with different crystallization temperatures and compared the crystal structures and absorption spectra. The result uncovered for the first time that α-form and δ-form have a clear correlation in terms of peak intensities in the range of 4 to 5 THz. If this spectroscopic method is established, it will not only be easier to estimate higher-order structures by absorption spectra, but it is also anticipated that it will pave the way in physics research towards the elucidation and control of higher-order structures of various biomass-based plastics, and the discovery of new functions.

Development Background

The research team leader, Associate Professor Seiichiro Ariyoshi, has long been interested in biomass-based plastic as a target for analysis, but thought it hard to approach as a material. However, Satoshi Ohnishi, then in the third year of his undergraduate studies (now in the first term of the first year of a master's degree program), was interested in biomass-based plastic, and although he sought Tsuji/Arakawa's laboratory, which is famous for PLA research, as his first choice during a laboratory selection survey for his senior thesis, he happened to be assigned to Ariyoshi's laboratory. Finding himself in that situation he thought to himself "Shall I try THz spectroscopy on PLA for my senior thesis?" This was the start of this research project. After Ohnishi acquired the first spectral data, efforts were made in earnest involving Professor Hideto Tsuji, Assistant Professor Yuki Arakawa, and Associate Professor Nobuya Hiroshiba of Osaka Institute of Technology, which led to this success. There are still a lot of matters to be investigated, but given that Ohnishi is dedicated to his research, it is natural that we have great expectations for the research.

Future Outlook

Although the above introduced only poly(L-lactide), PLA is generally known to form stereocomplexes by mixing enantiomers (poly(L-lactide) and poly(D-lactide)). Based on the knowledge and findings to date, the research team expects to expand their observation targets into enantiomers in the future and further be able to approach the origin of biomass-based plastic functional properties by comparing the progression of biodegradability and degradation caused by microbes and characteristic absorption spectra that appear in the THz range.

Reference

Seiichiro Ariyoshi, Satoshi Ohnishi, Hikaru Mikami, Hideto Tsuji, Yuki Arakawa, Saburo Tanaka and Nobuya Hiroshiba, “Temperature dependent poly(l-lactide) crystallization investigated by Fourier transform terahertz spectroscopy”, *Materials Advances*, **2**, 4630 (2021). DOI: 10.1039/d1ma00195g

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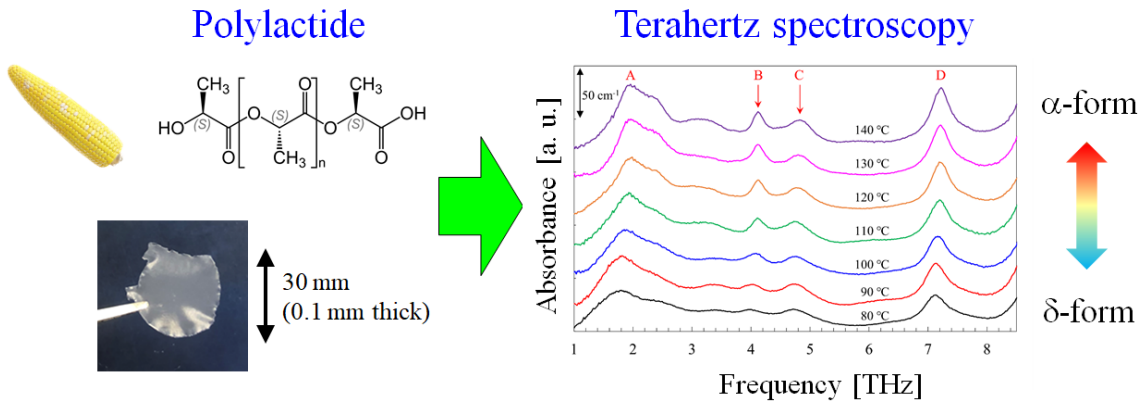
Figure1:



Title: A process from sample preparation through spectroscopic evaluation

Caption: Chemical composition and sample of PLA (Left)

THz absorption spectra of PLA for different crystallization temperature (Right)

Keywords: Crystal structure, Life sciences, Polymer architecture, Crystal plasticity, X ray diffraction