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Investigation of Deterioration Analysis of Biodegradable Poly(butylene succinate) using bench-top MALDI-TOFMS and Statistical Analysis

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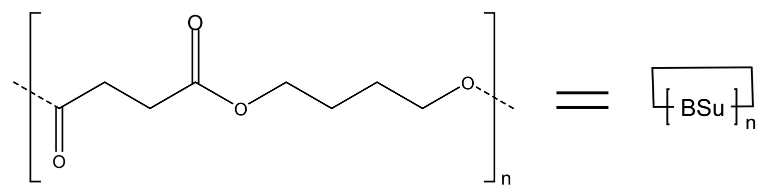
1. Introduction

In recent years, the accumulation of plastic waste has been recognized to have an adverse effect on ecosystems and the environment. One solution for this is to replace widely-used consumable plastics with biodegradable ones. Poly(butylene succinate) (PBSu) is used as one of the materials for biodegradable plastics. PBSu is often used for biodegradable straws and could be discarded in the environment. Investigating the biodegradability of PBSu is important to understand the properties of this polymer.

Here, deterioration of biodegradable PBSu buried in the soil for approximately two years was evaluated using bench-top MALDI-TOFMS, statistical analysis, and DSC.

✓ **Structural formula of the cyclic oligomer PBSu[1])**



✓ **Variations of end-terminal group in the linear oligomer of PBSu[1])**

- H-[BSu]$_n$-OH
- H-[BSu]$_n$-O(CH$_2$)$_2$CH=CH$_2$
- HOCO(CH$_2$)$_2$CO-[BSu]$_n$-OH
- H-[BSu]$_n$-O$^-$Na$^+$
- H-[BSu]$_n$-O(CH$_2$)$_4$OH
- HOCO(CH$_2$)$_2$CO-[BSu]$_n$-O$^-$Na$^+$
- Na$^+$$^-$OCO(CH$_2$)$_2$CO-[BSu]$_n$-O$^-Na^+$

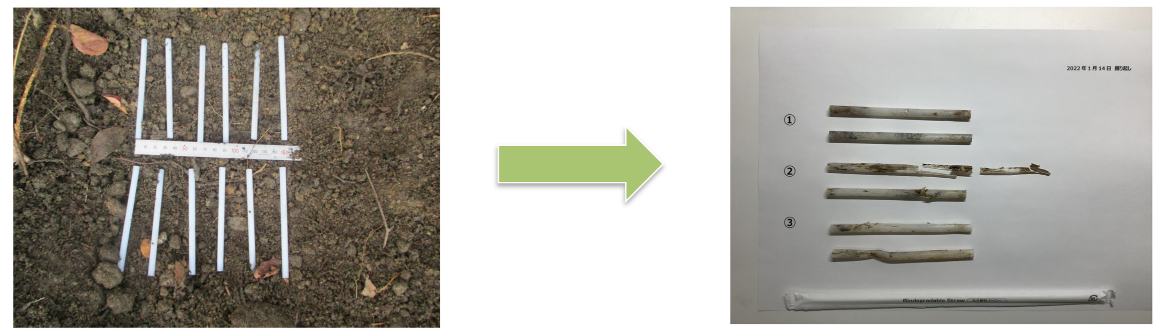
2. Methods

2-1. Locations of the buried biodegradable straws

The biodegradable straw made from PBSu were purchased from an online store. We buried the biodegradable straws at the following three locations in the "Shimadzu Forest" of the headquarters : I) high humidity, II) high microbe activity, III) long term exposure to sunlight. In addition to the buried straws, an untreated straw was measured for comparison.

Fig.1 An aerial photograph of "Shimadzu Forest" of the headquarters.

The biodegradable straws were dug up after approximately two years and these were clearly deteriorated. However, the degree of deterioration could not be determined by visual inspection.



Immediately before burying in the soil. After approximately two years

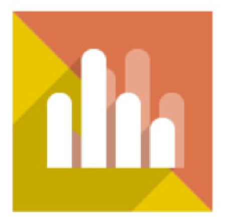
Fig.2 Deterioration of biodegradable straws by burying in the soil approximately two years.

2-2. Mass Spectrometry & Thermal Analysis

Each of the straws was prepared at 10 mg/mL in 1:1 (vol/vol) chloroform/hexafluoro-2-propanol. The sample solutions were mixed with DCTB and NaI as cation reagent, then 1 µL of each solution was subjected to analysis. Bench-top MALDI-TOFMS (MALDI-8020, Shimadzu Corporation) and statistical analysis software (eMSTAT Solution™, Shimadzu Corporation) were applied to discrimination of the degraded straws obtained from three different conditions and the untreated straw. In addition, differential scanning calorimetry (DSC-60Plus, Shimadzu Corporation) was applied to evaluate the difference in thermal characteristics of each sample.

MALDI-TOFMS "MALDI-8020"

- **Linear TOF**
- **Rapid MS analysis**
- **Polymer profiling**



eMSTAT Solution ; statistical analysis software

DSC "DSC-60Plus" ; Evaluation of thermal characteristic

3. Results & discussion

3-1. DSC

Differences in thermal properties of each sample were evaluated by DSC.

Fig. 3 shows the DSC curve obtained at temperature from -35°C to 250°C. Among various peaks in the curve, there were clear differences at the glass-transition temperature in the range from 30°C to 40°C and the endothermic peak near 150°C. The glass transition temperature was lower in buried straws compared to the untreated one and it can be seen from the enlarged view that sample exposed to sunlight has an inflection at 52.0°C (black arrow). The endothermic change around 150°C shows close 2 peaks (yellow box). Considering relative height of each peak, the 1st peak is larger in untreated straw and the 2nd peak is larger in the others.

Among the three buried samples, the sample exposed to sunlight shows the biggest difference to the untreated straw. The differences of thermal properties in each sample were evaluated in terms of a whole polymer by DSC. But since the detailed differences in chemical structure are unknown, MALDI measurements were performed.

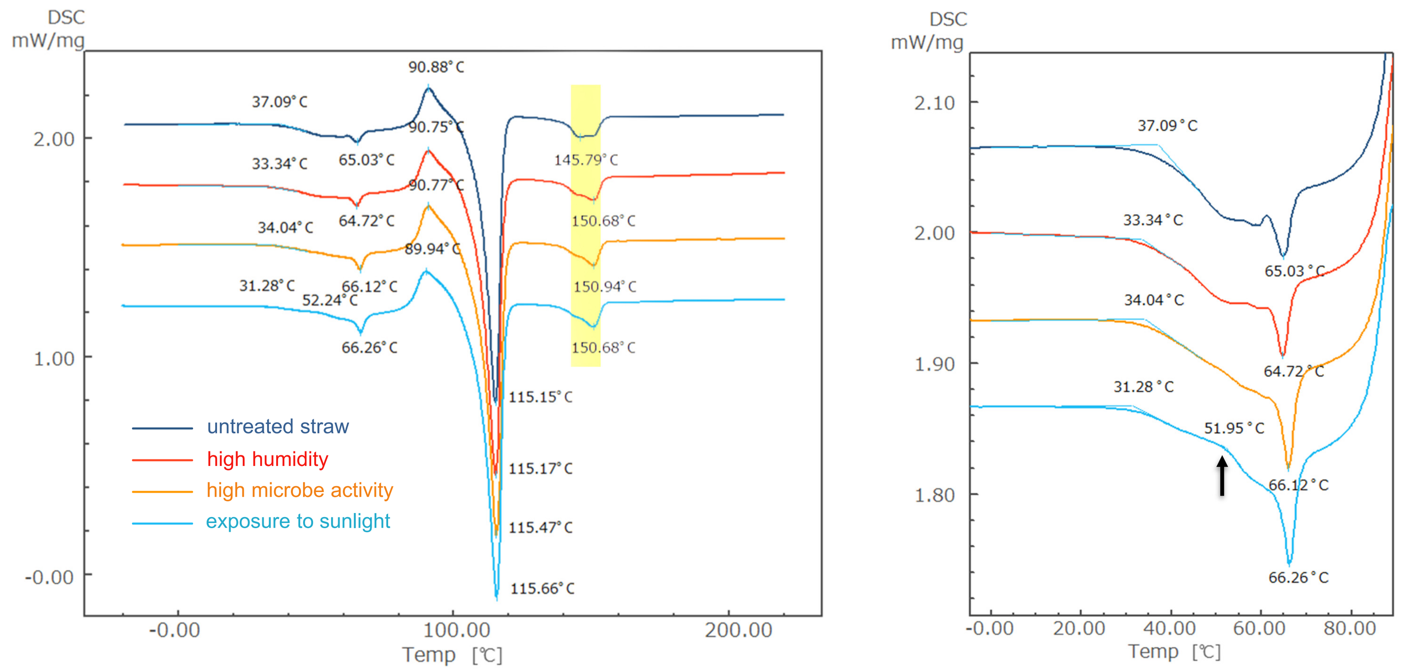


Fig.3 DSC curve obtained at temperature from -35°C to 250°C and the enlarged view around the glass transitions.

3-2. MALDI-TOFMS and statistical analysis

Using MALDI-TOFMS, multiple series of a polymer with 172 Da gap, which corresponds to monomer unit of PBSu, were observed. All signals were assigned as [M + Na]$^+$ according to a previous paper[1)]. The main signals were assigned to cyclic oligomers of PBSu. The minor signals derived from linear oligomers of PBSu were observed between the signals of the cyclic oligomers. The linear oligomers of PBSu had several variations attributed with the different combinations of both end-terminal groups.

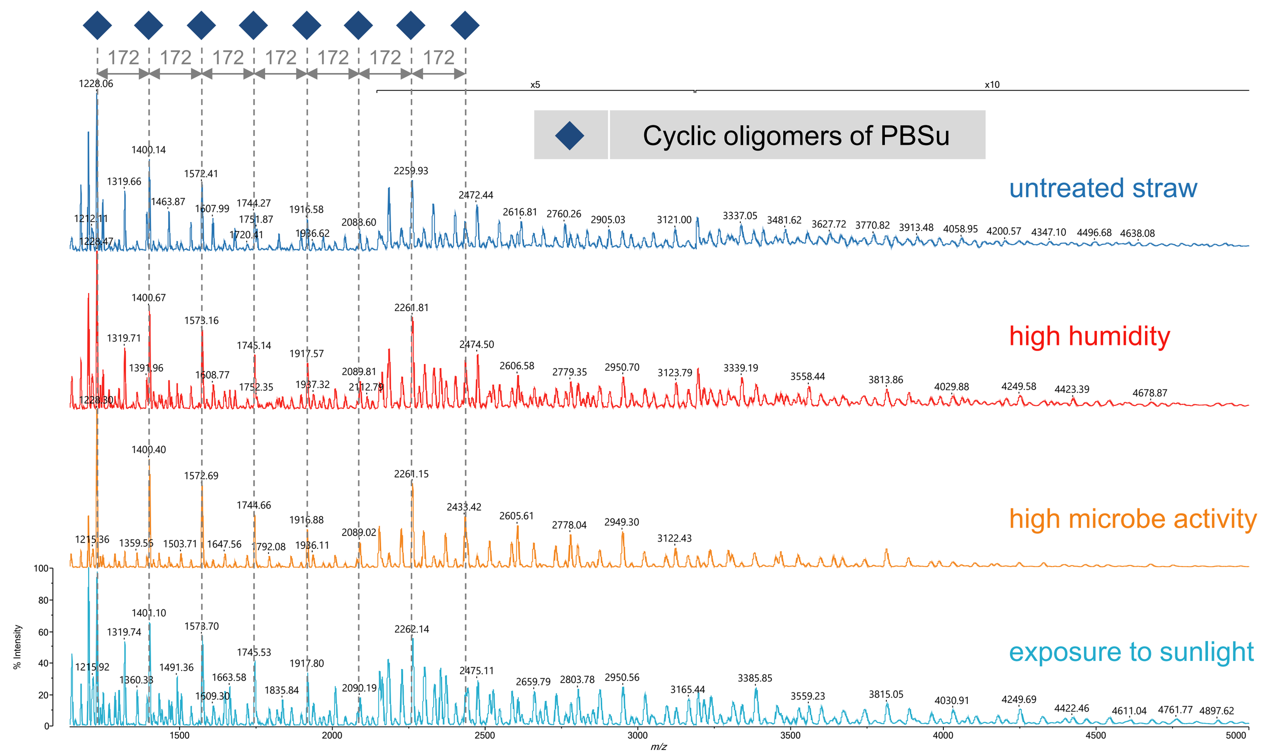


Fig.4 Comparison of mass spectra of PBSu oligomers under three different conditions.

The acquired data were subjected to statistical analysis and were processed with multivariate analysis (algorithm : PLS-DA). By performing multivariate analysis, they were classified into four groups, which suggested that the untreated straw and those buried in the "Shimadzu Forest" could be distinguished according to the degree of deterioration.

The PLS-DA loading plot revealed many peaks that contribute to the separation, in particular some peaks which were further away from the origin. Typically, *m/z* 1491.0 and 1663.1 were shown to contributed greatly to the separation in the loading plot.

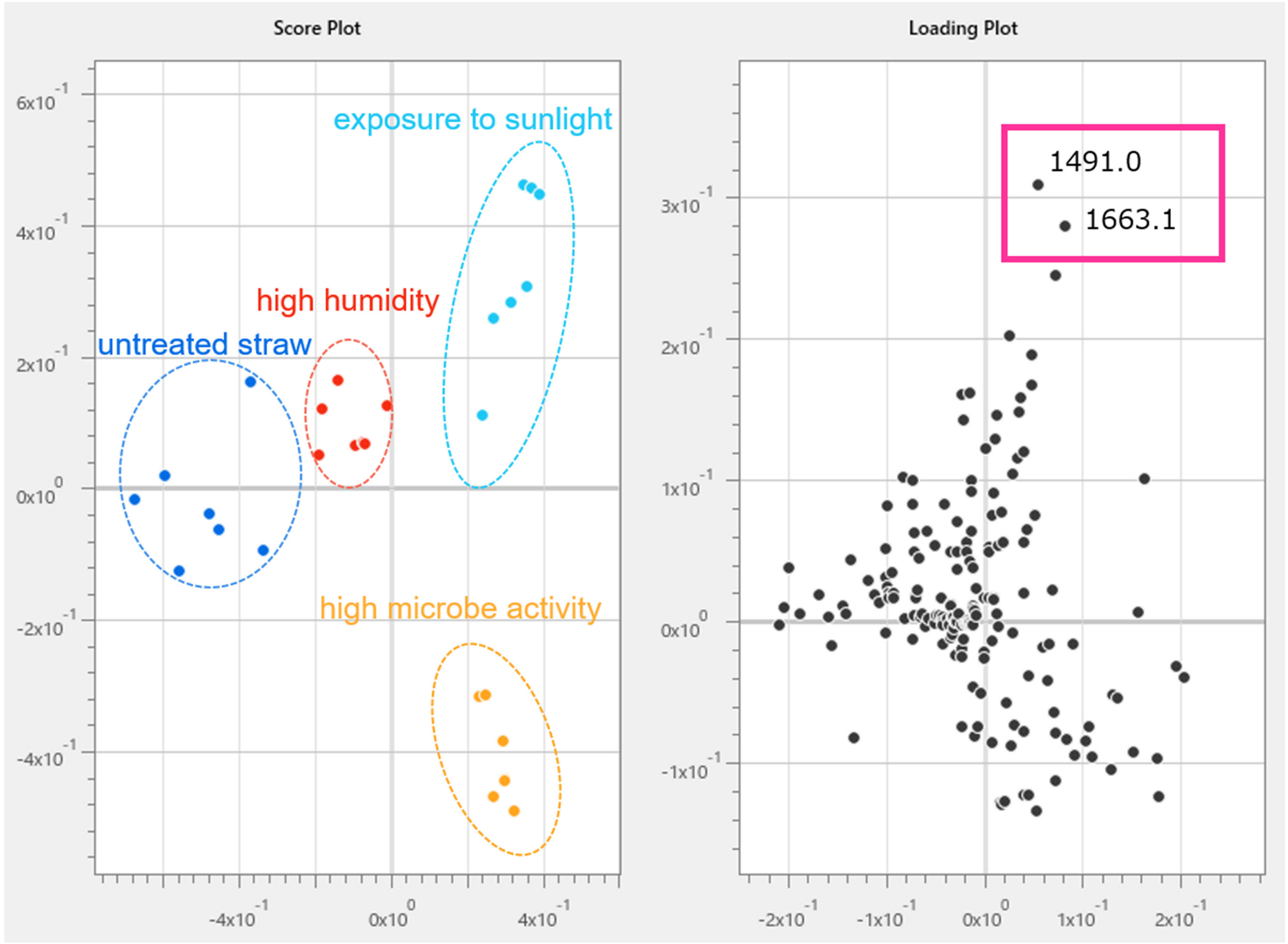


Fig. 5 Score Plots and Loading Plots in PLS-DA

Analysis of variance (ANOVA) of the *m/z* 1491.0 marker were conducted (Fig. 6). The p-value acquired by ANOVA and the box plot of the *m/z* 1491.0 marker demonstrated the statistical significance of this marker for the group separation.

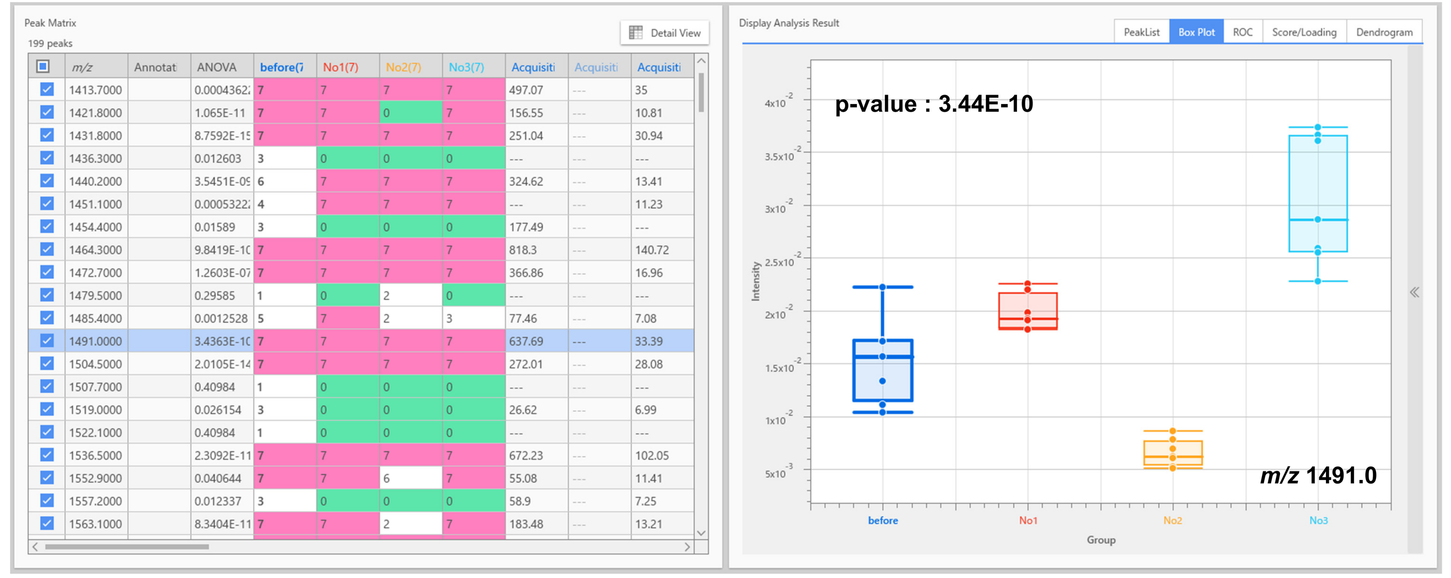


Fig.6 Results of ANOVA and the box plot of the *m/z* 1491.0 marker

Fig. 7 showed mass spectra at the *m/z* range from 1390 to 1750. The *m/z* 1491.0 and 1663.0 which contributed to the classification were assigned as [H-[BSu]$_n$-O(CH$_2$)$_4$OH + Na]$^+$ (n=8, and 9, respectively).

As a result, there was a clear difference of the intensity of [H-[BSu]$_n$-O(CH$_2$)$_4$OH + Na]$^+$ of the untreated straw and those buried in the "Shimadzu Forest", especially in the case of high microbe activity and exposure to sunlight. This suggests the same trend in results as for DSC measurement.

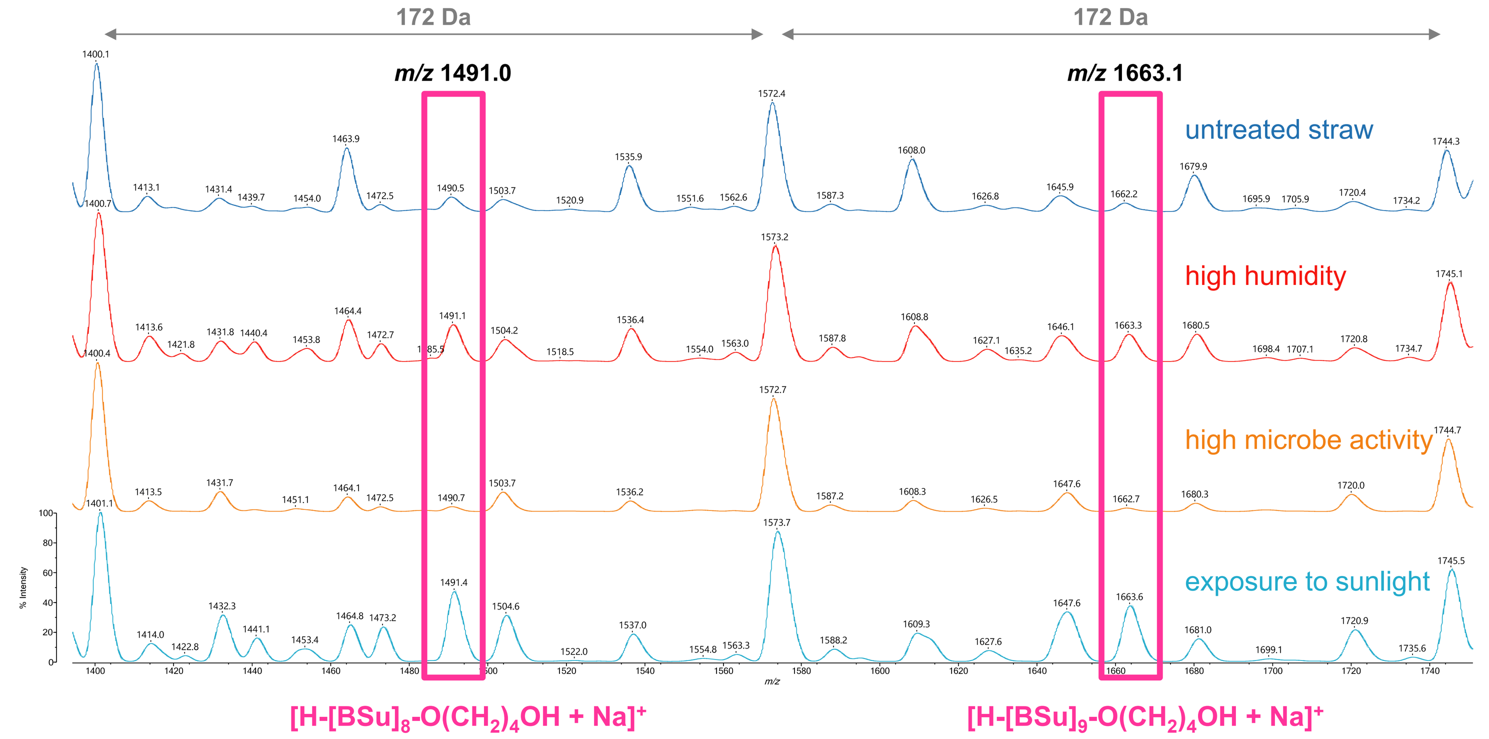


Fig.7 Mass spectra at the *m/z* range from 1390 to 1750

4. Conclusion

- Thermal characteristics by DSC can contribute to the evaluation of deterioration characteristics of a whole biodegradable plastic.
- The combination of useful bench-top MALDI-TOFMS and rapid statistical analysis enable to evaluate some changes in chemical structure of the biodegradable plastic.
- The MALDI-8020 and DSC are a useful combination to evaluate the characteristics of biodegradable plastics.

5. Reference

1) *Rapid Commun. Mass Spectrum.* **2013**, 27, 2213-2225.