

Characterization of Biodegradable and Oxo-Biodegradable Plastic Bags

□ Introduction

Plastics are commonly made of petroleum-based polymers such as low density polyethylene (LDPE), high density polyethylene (HDPE), polypropylene (PP) and polystyrene (PS) [1]. They are widely used due to their low cost, durability and versatility. However, most plastics are non-biodegradable, and has become a major environmental issue since they can remain as waste in the environment for a very long time [2], or break down to become microplastics. As an alternative, different plastic products such as oxo-biodegradable (O-BD) and biodegradable (BD) plastics have been introduced in the market.

Oxo-biodegradable plastics are also made of petroleum-based polymers and contain additives that break the structure of polymeric chain in the presence of light and oxygen via oxidation mechanism [1]. As conventional plastics are not biodegradable in nature, interest in the development of biodegradable plastics has grown over the years. Starch has been considered as a good candidate to produce biodegradable plastics since it is renewable, biodegradable, and has low cost [3].

This application news describes the use of Fourier Transform Infrared spectrometry (FTIR), Differential Scanning Calorimeter (DSC) and Thermogravimetric Analyzer (TGA) for characterization of plastic bags, which are labelled either as oxo-biodegradable or biodegradable.

□ Experimental

The samples used were commercially available plastic bags. There were three plastic bags labelled as oxo-biodegradable (O-BD), two plastic bags labelled as biodegradable (BD), and a plastic bag made from conventional polyethylene (PE) polymer as shown in Figure 1. The plastic bags were analysed using FTIR, DSC and TGA.

FTIR

The samples were measured using Shimadzu FTIR, IRSpirit™, and attenuated total reflectance (ATR) accessory with diamond prism (Figure 2). The measurement conditions are shown in Table 1.



Fig. 1: Labels of Plastic Bag Samples

Table 1: FTIR Measurement Conditions

Instrument	: IRSpirit, QATR-S (Diamond)
Wavenumber Range	: 4000 – 500 cm ⁻¹
Resolution	: 4.0 cm ⁻¹
Accumulation	: 16
Apodization function	: Happ-Genzel
Detector	: DLATGS



Fig. 2: IRSpirit™ FTIR with QATR™-S

DSC

The melting temperature (T_m) and % crystallinity were determined according to ISO 11357-3 [4]. The sample was cut into small pieces, sealed in an aluminium pan and then transferred to the Shimadzu DSC-60 Plus (Figure 3) furnace in Nitrogen gas atmosphere (100 mL/min). An empty aluminium pan was used as reference. The sample was heated to 180 °C at 20 °C/min and held for 5 minutes to erase thermal history. The sample was then cooled at -20 °C/min to 30 °C with liquid Nitrogen and held for 5 minutes before it was re-heated to 180 °C. Each sample was analysed at least 2 times.

TGA

TGA was used for compositional analysis based on ASTM E1131 [5]. About 20 mg of sample was placed in an alumina macro pan and analysed in a simultaneous DTA-TGA model DTG-60 (Figure 3) with an empty alumina macro pan as reference. The measurement conditions are shown in Table 2. Each sample was analysed at least 2 times.



Fig. 3: DTG-60 (left) DSC-60 Plus (right)

Table 2: DTG-60 Analytical Conditions

Component	Heating Rate (°C/min)	Analysis Range (°C)	Hold Time (min)	Gas Atmosphere (100 mL/min)
Highly Volatile (HV)	10	Ambient to 150	0	Nitrogen
Medium Volatile (MV)	10	150-600	0	Nitrogen
Combustible (C)	10	600-750	1	Air
Ash (A)	10	750-800	0	Air

Results and Discussion

Figure 4 shows the IR spectra of the plastic bag samples. The IR spectra of O-BD1, O-BD2, O-BD3 and BD1 were quite similar to IR spectrum of PE, having peaks from polyethylene. However, there were peaks, marked by arrows, in the IR spectra of O-BD1, O-BD2 and BD1 which were not observed in the IR spectrum of PE. This indicates that beside containing polyethylene, O-BD1, O-BD2 and BD1 may contain inorganic fillers. A comparison with IR library spectrum indicates that the inorganic filler could be calcium carbonate (CaCO₃) as shown in Figure 5.

For O-BD3, the IR spectrum was similar to the IR spectrum of PE, and did not seem to contain inorganic fillers. For BD2, a comparison with IR library spectrum shows that it contained mainly starch as shown in Figure 6.

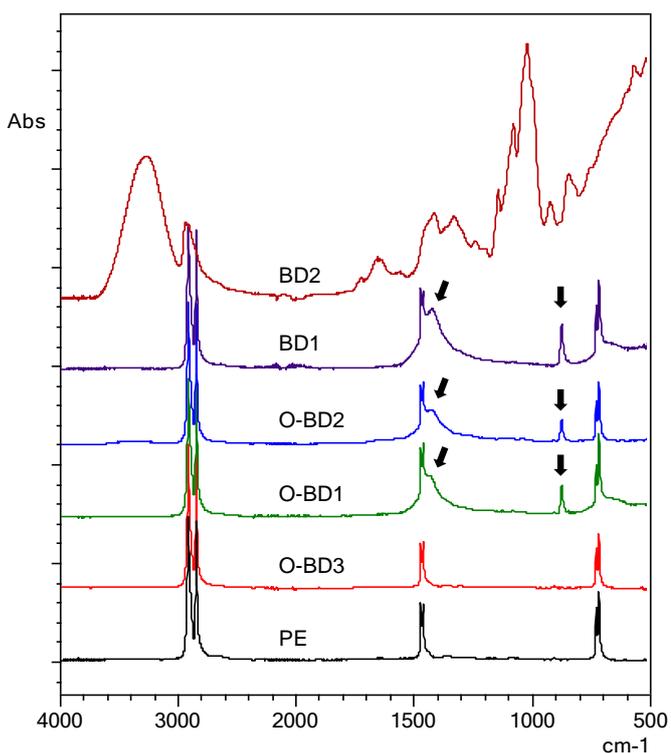


Fig. 4: IR Spectra of Plastic Bag Samples

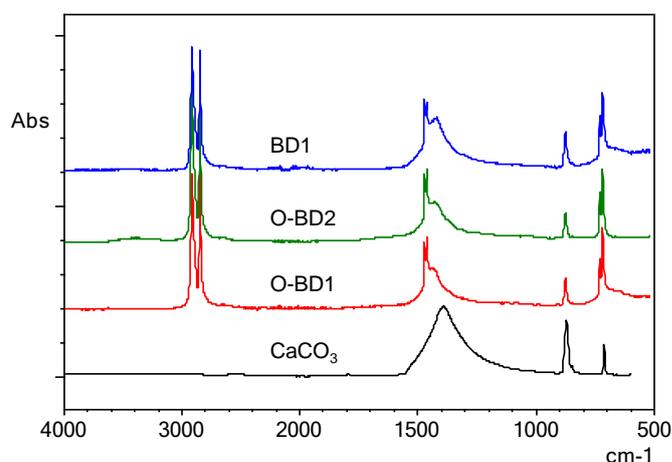


Fig. 5: IR Spectra Comparison of O-BD1, O-BD2, BD1 and CaCO₃

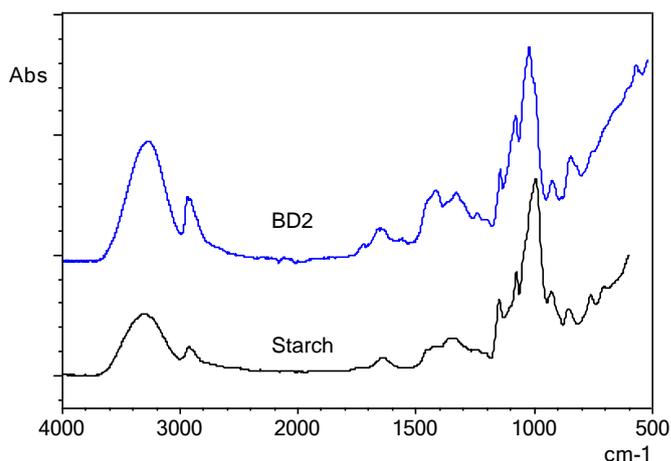


Fig. 6: IR Spectra Comparison of BD2 and Starch

The DSC graphs are shown in Figure 7 and the data is summarized in Table 3. The T_m between the various O-BD and BD1 plastic bags are almost similar to PE at about 130 to 134 °C. This shows that all plastic bags except BD2 may contain PE which correlate with their IR spectra (Figure 4). BD2 didn't undergo any melting like PE because it contains mainly starch (Figure 6).

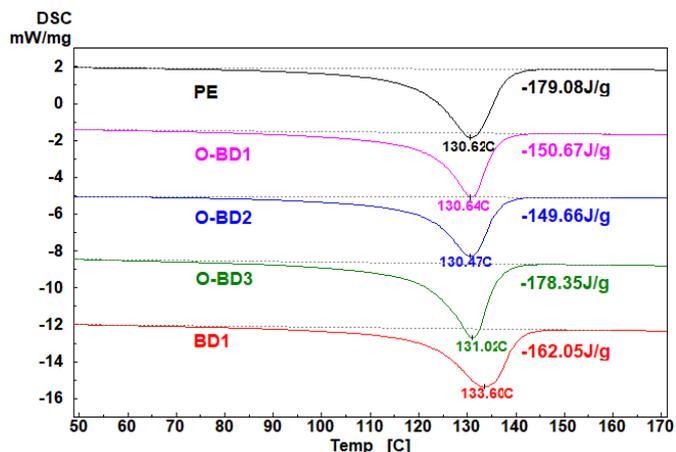


Fig. 7: DSC Graphs of Plastic Bag Sample

Table 3: Melting Results and % Crystallinity^A

Sample	Tm (°C) ^B	Hm (J/g) ^C	% Crystallinity ^D
PE	132.0	175.68	60.0 % ^E
O-BD1	131.3	151.19	59.4 % ^E
O-BD2	130.2	148.58	56.7 % ^E
O-BD3	131.2	175.81	60.0 % ^E
BD1	133.4	160.05	64.5 % ^E
BD2	PE melting peaks were not detected		

Notes

A = the data from 2 measurements were used for calculation

B = melting temperature (peak)

C = melting enthalpy

D = $(Hm / Hm \text{ for } 100\% \text{ crystalline PE}) \times 100 \%$
 = $(Hm / 293 \text{ J/g}) \times 100 \%$ [6]

E = same as D and based on "% MV" component in Table 4

The TGA graphs from DTG-60 analysis are shown in Figure 8 and the data is summarized in Table 4.

Table 4: Compositional Analysis Results^A

Sample	% HV	% MV	% C	% A
PE	< 0.1	98.9 - 99.1	< 0.1	0.9
O-BD1	< 0.1	86.9	5.0	8.1
O-BD2	0.2	89.4	4.8	5.6
O-BD3	0.2	99.6 - 99.8	< 0.1	< 0.1
BD1	0.2	85.7	5.8	8.3
BD2	11.4	74.8	10.0	3.8

Notes

A = the data from 2 measurements were used for calculation

In ASTM E1131 [5], "HV" indicates moisture, and other low-boiling (< than 200 °C) components whereas "MV" represents components such as oil and polymer that can degrade at 200 to 600 °C. "C" contains non-volatile oxidizable components such as carbon and "A" consists of non-volatile residues that oxidizes such as metal, filler, etc.

In PE, the "MV" component was almost 100 % as most of the polymer has decomposed at 600 °C. The "C" and "A" components of less than 1 % showed negligible inorganic components in these bags. This could be due to the lack of inorganic fillers or catalysts.

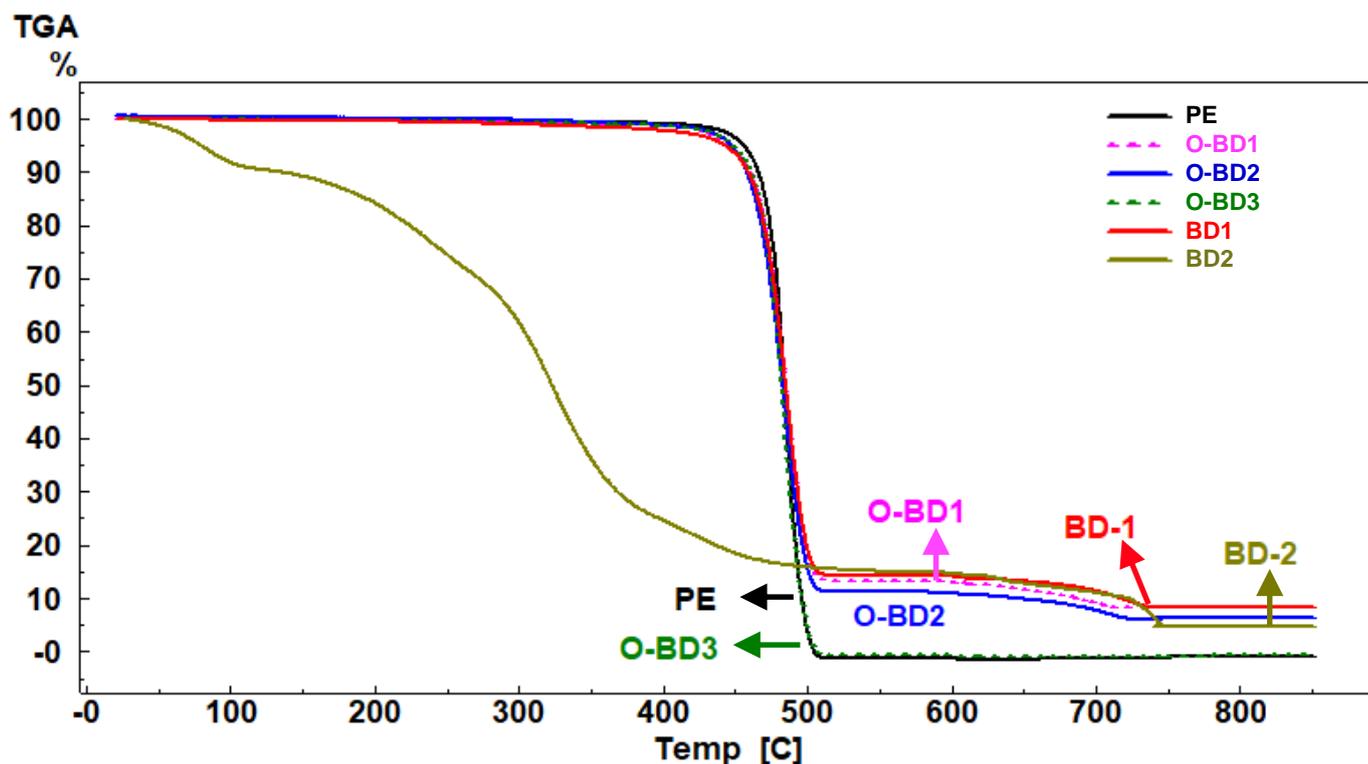


Fig. 8: TGA Graphs of Plastic Bag Samples

The TGA graphs for O-BD1 and O-BD2 were almost similar. In O-BD1 and O-BD2, 86.9 % and 89.4 % of polymer degraded at 600 °C respectively (Table 4, “MV” content). Both O-BD plastic bags also contained ~ 5 % “C” which could indicate the presence of other components that could only degrade in oxidative atmosphere. O-BD1 and O-BD2 contained 8.1 % and 5.6 % “A” respectively – “A” could most likely be metal salt additives that catalyse the degradation of plastic materials or inorganic fillers.

The TGA graph for O-BD3 was different from O-BD1 and O-BD2. In addition, O-BD3 has almost similar composition as PE. O-BD3 also has “A” of less than 0.1 % and probably doesn’t contain metal salt additives or fillers. Further tests should be carried out whether O-BD3 would degrade in the same manner as PE or O-BD bags.

BD1 has almost similar TGA graphs and composition as O-BD1 and O-BD2, which is consistent with their IR spectra (Figure 4). Further tests should be carried out to verify whether it is a BD or O-BD bag.

For BD2, there was rapid loss of weight from ambient to 150 °C in the TGA graph and the “HV” component of 11.4 % was the highest among all samples. This is most likely due to evaporation of water in starch [7]. The “MV” or cellulose content was 74.8 %. The “C” component of 10.0 % in BD2 likely represents the oxidative thermal decomposition of charcoal/carbon produced at 600 °C. BD2 also contained 3.8 % “A” non-volatile oxidizable residues such as fillers.

□ Conclusion

By using IRSpirit with ATR, DSC-60 and DTG-60, it is possible to differentiate the plastic bags labelled as biodegradable and oxo-biodegradable. Two oxo-biodegradable labelled plastic bags were found to have similar composition as biodegradable plastic bag. However, the third oxo-biodegradable labelled bag was found to have similar composition as that of conventional plastic bag, and would require further tests on its’ biodegradation behaviour.

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□ References

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