Determining the bio-based content of bio-plastics used in Thailand by radiocarbon analysis

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Abstract. Presently, there is an increased interest in the development of bio-plastic products from agricultural materials which are biodegradable in order to reduce the problem of waste disposal. Since the amount of modern carbon in bio-plastics can indicate how much the amount of agricultural materials are contained in the bio-plastic products, this research aims to determine the modern carbon in bio-plastic using the carbon dioxide absorption method. The radioactivity of carbon-14 contained in the sample is measured by liquid scintillation counter (Tri-carb 3110 TR, PerkinElmer). The percentages of bio-based content in the samples were determined by comparing the observed modern carbon content with the values contained in agricultural raw materials. The experimental results show that only poly(lactic acid) samples have the modern carbon content of 97.4%, which is close to the agricultural materials while other bio-plastics types are found to have less than 50% of the modern carbon content. In other words, most of these bio-plastic samples were mixed with other materials which are not agriculturally originated.

1. Introduction

Nowadays, the usage of plastic is increased due to the increase in population. Materials or equipments made from certain kinds of plastic can be recycled, while some cannot. Normally, plastic that has major uses in everyday life is disposable or is used only once then tossed away. This leads to the increasing problems of plastic garbage management because plastic garbage is quite difficult to eliminate from the environment [1]. Leaving or burying plastic garbage, the current approaches for spontaneous degradation, could take a very long duration up to hundreds of years. Moreover, certain kinds of plastic are hardly self-degradable and must be processed to degrade them. The processes, e.g., burning, can result in environment pollution [2]. The critical solution for this plastic material management is to make the plastic self-degradable in a short duration so that it does not pollute the environment. The production of bio-plastics is one of the approaches to solve the problems. Bioplastics are made from biodegradable agriculture products, for instance, sugarcane and tapioca, which can be degraded in a short period of time and are environmentally friendly [3]. Most importantly, these bio-plastic materials are made from plants that can be grown as many as desired, i.e. renewable, unlike the petrochemical plastics made from hydrocarbon-based fossil materials that take very long time to produce and cause pollution in the production processes. This is the main reason why bioplastics are increasingly gaining attention in the market. However, the amount of agricultural materials contained in the bio-plastics product can be specified by the amount of modern carbon in bio-plastics. Therefore, this research aims to determine the modern carbon in bio-plastic commercially available in Thailand market using the carbon dioxide absorption method.

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Bio-based content analysis is one of the methods of bio-plastic testing. The bio-based content is defined as the ratio of the weight of the bio-based carbon in material to that of the total organic carbon in the product [4]. The value obtained from the analysis is the ratio of the combination between bio-plastic and petroleum plastic contents. If the plastic comes from 100% bio-plastic, the C-14 amount would be equal to the natural C-14 ratio. If the plastic content comes entirely from petroleum, there would be no C-14. In this present study, we aimed to examine the bio-plastic materials in Thailand in order to determine the bio-based content using the carbon absorption method.

In the present study, the plastic samples from the disposable plastic container produced in Thailand were analysed for C-14 ratio. This analysis method can be applied to all carbon-based products and was approved by American Society for Testing and Material (ASTM) No. ASTM 6866. Furthermore, there are many studies that proved that this method is simple, accurate and achievable [5,6,7]. The analysis method employed can be either accelerator mass spectrometry (AMS), benzene synthesis or carbon absorption. In the previous study by Noakes et al. [8], all three methods were evaluated and it was found that the most accurate method was AMS and that the benzene synthesis and carbon absorption methods had lower accuracy, respectively. The accuracy of all analysing methods, however, was acceptable. Culp et al. compared the accuracy and precision of C-14 between natural products and bio-based materials analysed by AMS and LSC. Results showed that degree of naturalness accurate and precise $^{14}C$ measurement is achievable by both methods [9]. The analysing method in this present study was performed using carbon absorption because of the simplicity of the process and the variation was acceptable. In the study by Molnar et al. [10], which fixed the parameters in order to minimize the variation of the carbon absorption analysing method, the minimized variation is found to be around 2 percent. Each of the three methods has its own advantages and disadvantages. However, when comparing the duration and cost of analysis, the carbon absorption method is the most preferred method in the industrial application.

2. Experimental

In this work, carbon absorption method was used for sample preparation. The process of this method [1] is as follows:

2.1. Samples and standard

Plastic samples in this present study are divided into two groups, which are plastic granules and commercial bio-plastic products. Plastic granules are divided into six types. The first four are bio-plastics, i.e. poly(lactic acid) (PLA), polybutylene succinate (PBS) type 1 and 2, thermoplastic elastomers and bio-TPE, and the other two are petroleum-based plastics i.e., polybutylene adipate-co-terephthalate (PBAT) and polypropylene (PP). Among nine samples for commercial bio-plastic products, five are Thai products (BP1-5), two are imported products (BPA from America, BPB from Australia), and the other two are research laboratory plastic products (BPX1, BPX2) with well-known composition which were added to this experiment as the reference for the efficacy of the test. The known standard materials were sugar with adjusted strength of the radiation as the Oxalic II (49960c) which is the reference for the substance that has natural C-14 amount before 1950 and marble as the background radiation reference.

2.2. Carbon dioxide preparation from samples

Plastic samples were in a solid form, so they had to be transformed into carbon dioxide gas before analysis using oxygen combustion bomb. The samples were combusted in high pressure of around 30 atm in the oxygen-provided combustion tank and electricity was used to ignite the combustion. The samples were prepared by transferring 8-10 grams of plastics into the container in the high pressure tank, then the electric circuit was completed by connecting the electrode on the tank lid to the plastic samples in the tank. The air in the tank was expelled using oxygen gas. The pressure was adjusted by the oxygen pump before the combustion started. After combustion, carbon dioxide gas from the samples was contained in the tank.

2.3. Carbon dioxide purification
Carbon dioxide from the combustion step had to be purified to eliminate the ions and the contamination by transporting the gas through the following 3 solutions:

- Potassium iodide and iodine (KI/I₂) for phosphorus, nitrogen, and sulfur oxides filtration.
- Silver nitrate solution (AgNO₃) for halide and acid precipitation.
- Potassium dichromate in sulfuric acid (K₂Cr₂O₇/H₂SO₄) for carbon monoxide (CO) and sulfur dioxide (SO₂) extraction.

The whole purifying system must be vacuumed before letting the carbon dioxide gas in. Moreover, after decontamination, the gas then passed through a container containing the solution between liquid nitrogen and alcohol in order to dehumidify by condensation. Then, the gas would be transformed into a solid form after passing through liquid nitrogen at the back of the system. All carbon dioxide was transported into the storage container.

2.4. Carbon dioxide absorption
Carbon dioxide was absorbed in the scintillation cocktail before undergoing modern carbon analysis by LSC. The scintillation cocktail was the compound between the Carbosorb and Permafluor scintillator in the equal ratio. In this experiment, 10 ml of Cabosorb was mixed with 10 ml of Permafluor. The cocktail was carefully prepared in the nitrogen atmosphere to avoid exposure of carbon dioxide to the air. The prepared cocktail was then injected into the glass tube connected to the gas absorption system in the suitable amount compared with the carbon dioxide sample. The system must be vacuumed before carbon dioxide injection, because the cocktail can absorb the carbon dioxide remaining in the gas absorption system. The absorption proceed was started by releasing the carbon dioxide gas from the storage container into the vacuum system in a preferred amount. Secondly, the cocktail-filled glass tube was connected to the system by open the valve on the top of the glass tube and the carbon dioxide gas was pumped to circulate in the system for 20 minutes. The carbon dioxide-adsorbed cocktail was then weighted for the adsorbed gas around 2.5-2.9 grams after subtraction the cocktail’s weight. The cocktail was transferred to the glass container for further analysis [11].

2.5. Carbon-14 analysis using liquid scintillation counter
The suitable counter is the low strength radioactive counter which is normally used in the measurement of naturally occurring radioactive material (NORM). The liquid scintillation counter measures the energy released from the radioactive substance which activates the fluorochrome to the excited state. The fluorochrome then emits the energy in the visible spectrum and this light can be measured by photomultiplier tubes. This instrument is able to measure the alpha ray and low-energy beta ray due to the high sensitivity. The efficiency of the measurement can be increased when using the cocktail combined with the sample [12].

2.6. Bio-based content determination
The calculation of bio-based content was performed by comparing the C-14 amount to that of the standard samples. All measurements were adjusted for the carbon isotope (δ13) which is C-13/C-12, the stable isotopes in all samples before bio-based content calculation. The standard value of VPBD was used [13]. The calculated values were then calculated for the modern carbon ratio from the equation 1 [14]:

\[
pMC = \frac{A_{sn}}{A_{on}} \times 100
\]

where
- \( pMC \) = Percent modern carbon
- \( A_{sn} \) = Normalized sample activity
- \( A_{on} \) = Normalized standard activity (Oxalic acid)
The obtained pMC values were then used to calculate the bio-based content as shown in the equation 2 [14]:

$$\text{Bio-based content} = \left( \frac{\text{pMC}_{\text{sample}}}{\text{pMC}_{\text{natural}}} \right) \times 100$$ (2)

where pMC_{\text{sample}} is the percent modern carbon of samples while pMC_{\text{natural}} is percent modern carbon of the raw agriculture material, representing the natural C-14.

3. Results
Percent modern carbon of the raw agriculture material represented the natural C-14 amount and the substance was used in the bio-based content calculation. In the present study, the sugar from sugarcane and cassava which are biomass materials, were selected to be the C-14 references. Table 1 shows that percent modern carbon values of both biomass materials were around 112 percent, and this value was set to be the reference for the 100 percent bio-based product substance [15]. Then, this modern carbon value of the agriculture product was compared to the values of other plastics to calculate the bio-based content. The efficiency of the liquid scintillation counter measurement was around 67 percent.

Table 1. Percent modern carbon and bio-based content of biomass materials

| Biomass material | pMC (N=3) | Bio-based content (N=3) |
|------------------|----------|------------------------|
| Sugarcane        | 112.15   | 100.00                 |
| Cassava          | 112.05   | 99.91                  |

The bio-based content of each sample is shown in Table 2. Results show that the bio-based content of PLA is 97.36 percent, which is closest to the content from the agriculture product, while that of Type 1 and 2 PBS and Bio-TPE is in the range of 40-50 percent. From the experiment, PLA is the only bio-plastic that its bio-based content is as high as that of the natural products. On the other hand, PBAT and PE resulted in bio-based content around 1-3 percent. All five bio-plastic products in Thailand have very low bio-based content around 2-7 percent. Bio-plastics from Thai bio-plastic laboratory have higher bio-based content at 52 and 56 percent. However, two imported bio-plastics display over 90 percent of bio-based content.

Table 2. Bio-based content of each bio-plastics

| Bio-plastics | Bio-based content (%) (N=3) |
|--------------|-----------------------------|
| PLA          | 97.36                       |
| PBS1         | 39.60                       |
| PBS2         | 45.22                       |
| Bio-TPE      | 46.53                       |
| PBAT         | 2.44                        |
| PP           | 1.91                        |
| BP1          | 4.78                        |
| BP2          | 6.30                        |
| BP3          | 6.11                        |
|    |     |     |
|----|-----|-----|
| BP4 | 2.93 | 1.60 |
| BP5 | 4.55 | 0.97 |
| BPX1 | 51.96 | 2.21 |
| BPX2 | 55.68 | 2.39 |
| BPA | 90.42 | 3.74 |
| BPB | 91.93 | 3.62 |

### 4. Conclusions and discussion

In this study, the modern carbon in bio-plastic was determined using the carbon dioxide absorption method to indicate how much agricultural materials are contained in the bio-plastic products commercially available in Thailand market. The results show that PLA was the only bio-plastic that was made entirely from agriculture material without synthetic plastic. This bio-plastic can be recognized as the whole bio-based content plastic. PBS and Bio-TPE were found to have less than 50 percent of bio-based content, thus the major composition of these materials are synthetic plastics. PBAT and PE products, which are petroleum-based synthetic plastics, showed a very low bio-based content and the measured values were comparable to the background radiation reference. While five Thai bio-plastic products were found to have very low (less than 10 percent) bio-based content, which is in contrast to the imported bio-plastic products that had more than 90 percent of bio-based content. This shows that bio-plastic products produced in Thailand have a very low composition of bio-based materials.

To validate the method of our analysing protocol, it is necessary to have a known standard reference of bio-plastic. For this study, imported BPA and BPB samples were used as references, with each having its bio-based content (%) shown on its label. This reference served as the known composition standard. The results of measurement value from BPA and BPB samples differed from the value stated on the label about 8.8 percent. This variation was comparable to the previous study by Culp Ret.al [9] and was less than the variation of the standard testing protocol which is 15 percent. In addition to protocol validity testing by comparing with the composition label, this study was also approved by the formulator of the bio-plastic produced for the research group. It was approved that the sample of the plastic container (BPX1) had the bio-based content of 51.96 ± 2.21 percent. Therefore, our protocol yielded the acceptable measurement value. The advantages of our protocol are the minimal analytical time which allows multi-type product analysis and the lower cost of analysis.

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