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Short communication

Biogenic fraction in the synthesis of polyethylene terephthalate

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ABSTRACT

The biogenic fraction of polyethylene terephthalate (PET) samples produced by direct esterification of terephthalic acid and ethylene glycol with antimony trioxide catalyst was evaluated by radiocarbon accelerator mass spectrometry. At the Radiocarbon Laboratory of Universidade Federal Fluminense, we measured PET samples of different biogenic fractions and the chemical components involved in the synthesis reactions. The percent modern carbon was determined and the biogenic fractions were calculated according to Standard Test Methods for Determining the Biobased Content of Solid, Liquid, and Gaseous Samples Using Radiocarbon Analysis (ASTM-D6866). Stable isotopes were measured by conventional mass spectrometry and revealed that isotopic fractionation may be taking place in the synthesis of PET. For the theoretical 20% biobased carbon sample, the radiocarbon result lead to a 23% biogenic fraction, in agreement with 3% uncertainty anticipated by the norm. The reasons for uncertainty in the specific case of PET are discussed and seem to lie on the presence of residual ethylene glycol within the PET structure.

1. Introduction

Lately, the concern with environmental aspects has motivated effort to produce all sorts of plastics from biogenic sources. Therefore, the production and control of biogenic fractions in this kind of material have an important role. Stable carbon isotopes technique can distinguish between petroleum sources and some biogenic sources, depending on the origin of its components. This technique is widely used to distinguish between woody plants and grass, since differences in photosynthetic metabolism lead to isotopic fractionation. The so-called C3 plants utilize the Calvin–Benson photosynthetic pathway and have lower $^{13}C/^{12}C$ ratios, leading to $\delta^{13}C$ values ranging from −32‰ to −22‰. The C4 plants use the Hatch–Slack cycle and have $\delta^{13}C$ values in the range of −17‰ to −9‰ [1].

Since petroleum sources have $\delta^{13}C$ values ranging from −40‰ to −28‰, stable isotopes technique can be used to distinguish it from C4 sources but cannot provide such an accurate determination of biogenic fraction for soy-based products, for example. Moreover, when dealing with unknown sources, this ambiguity cannot be sorted out.

In the last decade, radiocarbon was used as a tool for determining biobased fraction in commercial products [2–6]. Fuels and polymers composed by a combination of fossil and biogenic raw materials can have its biogenic fraction determined since fossil materials have no radiocarbon. This technique is therefore only capable of distinguishing fossil from biogenic sources and providing a means of monitoring the reactions involved in the production of industrial materials. The ASTM-D6866 norm has been widely used to determine the biobased content of solid, liquid and gaseous samples using radiocarbon analysis. Nevertheless, it is worth discussing the particularities of each material as well as the chemical reactions that take place.

In this work, we report the use of the radiocarbon signature to understand the synthesis of polyethylene terephthalate (PET), a thermoplastic polymer resin of the polyester family used in synthetic fibers as well as in consumer goods packaging. PET is one of the most produced thermoplastics in the world thanks to its excellent mechanical and thermic properties associated to the low production cost [7]. In Brazil, the main application of PET is in packaging industries with 71% of the production [8]. The high prices of oil associated to environmental concerns have stimulated the search for sustainable alternatives.

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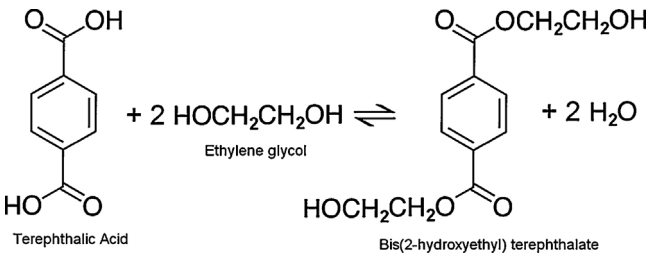

Fig. 1. Scheme of esterification of terephthalic acid with ethylene glycol.

Although 100% biobased polymers can be synthesized, inferior mechanical properties as compared to petroleum-derived materials are a concern in the development of renewable materials [9]. Biobased PET can be derived from different biomass. Partly biogenic PET will be the product of biogenic ethylene glycol (EG) and fossil terephthalic acid (TA).

2. Materials and methods

For the synthesis of polyethylene terephthalate, the direct esterification of terephthalic acid (TA) with ethylene glycol in the presence of antimony trioxide catalyst was used. This chemistry route, used in most of the new worldwide PET facilities, is represented in Figs. 1 and 2. In the esterification of terephthalic acid and ethylene glycol, bishydroxyl ethyl terephthalate (BHET) is produced as the main monomer for polycondensation (Fig. 1). In the reversible reaction, water (as a side product) should be extracted in order to increase conversion yield [10]. In the polycondensation step, oligomers and polymer chains undergo reaction to produce a longer polymer (Fig. 2). Ethylene glycol is the byproduct and should be removed to increase the rate of polycondensation and the chain length [10].

Fossil ethylene glycol (>99.5% chemical purity) was purchased from Sigma-Aldrich (Vetec) as well as fossil purified terephthalic acid (>98% chemical purity) and antimony trioxide (>98% chemical purity). Biobased ethylene glycol (>99.8% chemical purity) was a gift from Oxiteno and biobased terephthalic acid (>92.2% chemical purity) was synthesized at the Petrobras Research Center. The chemical impurities in the latter would also be from biogenic origin and would be any sort of incomplete TA molecules (e.g. p-xylene, p-tolualdehyde, p-toluic acid or 4-carboxybenzenaldehyde). All chemicals were used as received without any further purification. In what concerns the origin of the biomass for the 100% biogenic components, EG was derived from sugarcane while TA was derived from soy. The harvest years are unknown.

The reactions were carried out in a 100 mL cylindrical glass flange reactor. On the cover of the reactor a packed column was fitted and then an air-cooled Allihn type partial-condenser to better control the column top temperature. At that point, a 45° derived Liebig type condenser cooled by water was attached. A graduated flask was used to collect and measure the level of by-products as an inference of the reaction extension. A vacuum pump was connected to the flask outlet.

Ethylene glycol (41.20 g) was weighed and added into the reactor. Antimony trioxide was added at a fraction of 245 ppm. The mixture, continuously flushed with inert gas, was heated to 60 °C and then smoothly stirred (anchor type) for the addition of the terephthalic acid (37.3 g). This step was done using a helical conveyor and lasted about 30 min. The reactive paste was stirred to 200 rpm and heated to its boiling point (197 °C) using a heating mantle. As water was produced and removed by the column, the boiling point of the mixture, mostly ester compounds, increased to 240 °C. At this point, the flow of inert gas was turned off, the temperature of the reactor was increased to 270 °C and vacuum was stepwise applied to the system. The polymerization was carried out for 2 h or until ethylene glycol production by the reaction stopped. The polymer was left to cool and solidify inside the reactor.

With the aim of producing partially biogenic PET, fossil terephthalic acid was combined with biogenic ethylene glycol from sugar cane. Assuming a complete reaction, a 31.25% biogenic in mass would be expected what would lead to the theoretical biogenic carbon fraction of 20%. Also, 100% fossil and 100% biogenic PET were synthesized.

At the Radiocarbon Laboratory of the Fluminense Federal University (LAC-UFF), we measured samples of 100% fossil, 20% biogenic carbon, 100% biogenic PET and the chemical components involved in the reactions. LAC-UFF is the only facility in South America so far to use the Radiocarbon Accelerator Mass Spectrometry Technique and has been developing research in several fields of science [11]. The present work is the first research on polymer biogenic fractions analysis completely performed in Brazil.

Fuel samples were frozen inside prebaked quartz tubes containing silver powder and cupric oxide in a dry ice/ethanol trap then pumped out in a liquid nitrogen trap. All samples were combusted at 900 °C for 3 h in a muffle oven. Combustion blank used was reactor graphite and reference material for quality control was IAEA C6 sucrose. The gas was purified by means of dry ice/ethanol traps in a stainless steel graphitization line [11]. For graphitization we used the zinc/titanium hydrate method with iron catalyst [12]. Individual torch sealed tubes were heated for 7 h in a muffle oven at 460 °C. Graphitized samples were pressed in each of the 40 cathodes wheel of the SNICS ion source and measured in the 250 kV Single Stage Accelerator System (SSAMS) of the Physics Institute. The isotopic fractionation was corrected by measuring the $\delta^{13}C$ on-line in the accelerator. Background was measured using processed graphite samples, which yielded average $^{14}C/^{13}C$ ratios of 6×10^{-13}. Average machine background was 10^{-13} for unprocessed graphite. Accuracy was checked by measuring reference materials within the 2-sigma range of consensus values.

Stable isotopes ratios were measured at Beta Analytic by conventional isotope ratio mass spectrometry (IRMS).

3. Results and discussion

Results of percent Modern Carbon are presented in Table 1. Based upon "method B" of ASTM-D6866 [13], the $^{14}C/^{12}C$ ratios were determined in relation to a primary standard SRM4990c, then multiplied by a factor 0.95 to correct for the bomb carbon, obtaining the "true" biobased content of the sample. This reference ^{14}C value in ASTM-D6866 was based on average atmospheric $^{14}CO_2$ values in 2010 as measured at only a few measurement sites in the world. Atmospheric $^{14}CO_2$ values are, however, variable in time (the annual decrease of global atmospheric $^{14}CO_2$ is approximately 0.5 pmC per year) and space (rural vs. more urban regions can differ more than 10 pmC), which makes this the chosen reference value for 2010, not necessarily representative for all plant materials from 2010, let alone, for plant-based materials of other harvest years. Hence, the ±3% (1-sigma) range, as given by ASTM-D6866 as uncertainty range for the determined biogenic carbon fraction, very realistically captures for most sample materials (incidentally larger anomalies will appear) the uncertainty in the used ^{14}C reference value for the biogenic carbon of the sample material.

Therefore, the ^{14}C values of biogenic TA, biogenic EG and biogenic PET may very well represent the ^{14}C value for 100% biogenic carbon of these materials, while the used ASTM reference value could be slightly higher and therefore has given biogenic carbon fractions between 98% and 100%, instead of 100%. The differences, in ^{14}C value between biogenic TA and biogenic EG, could be related to the use of plant materials from different harvest years.