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Cellulose acetate butyrate as multifunctional additive for poly(butylene succinate) by melt blending: Mechanical properties, biomass carbon ratio, and control of biodegradability

Yuya Tachibana [a], Nguyen Thien Truong Giang [a,b], Fumi Ninomiya [a], Masahiro Funabashi [a], Masao Kunioka [a,*]

[a] National Institute of Advanced Industrial Science and Technology (AIST)/1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan
[b] National Institute of Animal Husbandry (NIAH)/Tu Liem District, Hanoi, Socialist Republic of Viet Nam

A R T I C L E I N F O

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A B S T R A C T

We have evaluated the plasticizing effect of poly(butylene succinate) (PBS) and cellulose acetate butyrate (CAB). PBS and CAB were mixed with a melt-kneading machine. The tensile strength and strain at break in the case of the blend with 10% CAB in the PBS matrix were 547% and 35 MPa. It showed that CAB acted as a plasticizer for PBS. The biomass carbon ratio of the blends measured by accelerator mass spectrometry based on ASTM D6866 showed that the biomass carbon derived from a part of the CAB corresponded to the theoretical value of the polymer blend. The biodegradation of PBS with the CAB melt blend powders was evaluated by a microbial oxidative degradation analyzer under controlled compost conditions based on ISO 14855-2. PBS with 10% CAB was not degraded within 60 days due to the addition of CAB that could control the biodegradability of the PBS.

1. Introduction

Aliphatic polyesters, such as poly(lactic acid), polycaprolactone, and poly(butylene succinate) (PBS), have received significant interest for industrial applications, such as agricultural mulch sheets to protect against insects, control growing weeds and maintain suitable conditions, such as temperature and moisture, for the better growth and effective production of vegetables [1,2]. It is important to control and inhibit the biodegradability during use, therefore chemical modification, the addition of a stabilizer, and polymer composites were employed. Furthermore, the flexibility of the material is an important property for end-use applications. The biodegradability of materials is also useful for the solution of waste problems, thus biodegradable materials are called environment friendly polymers.

PBS resins are commercially available biodegradable materials [3,4]. One of these is available under the tradename "Bionolle®" based on the polycondensation of 1,4-butanediol and succinic acid by a Japanese company (Fig. 1.) [5]. However, other properties of PBS, such as softness, tensile and gas barrier properties, melt viscosity for further processing, etc., are frequently insufficient for various end-use applications. To modify its properties, some methods such as an additive, inorganic filler, nanocomposite, and other polymer were developed [6]. In addition to its biodegradability, PBS has recently been produced from biorenewable resources to reduce greenhouse gas emissions and provide sustainable alternatives to the reliance on limited petroleum-based resources. The Showa High Polymer Co. [7] and Mitsubishi Co. [8,9] are now also establishing the production of succinic acid as one of the monomers of PBS from biomass resources, and a partially-biobased PBS is produced. We developed a fully biobased PBS from the biobased furfural [10]. To promote high biobased materials, it should be required to use the additives derived from renewable materials.

Cellulose esters are one of the thermoplastics derived from biomass feedstocks. Cellulose acetate butyrate (CAB) esterified by acetyl and butyryl groups (Fig. 1.) is a brittle and transparent material. Therefore, CAB has been used as a photofilm and a coating material. Some researchers reported that CAB acted as a plasticizer for some polyesters, such as poly(hydroxy butyrate) [11–13]. We reported that biobased furfural was a good plasticizer for PBS [14]. Ogata et al. produced the cast film of CAB which contained PBS as a plasticizer [15]. The CAB cast films containing PBS obtained using

* Corresponding author. Tel.: +81 29 861 4584; fax: +81 29 861 4589.
E-mail address: m.kunioka@aist.go.jp (M. Kunioka).

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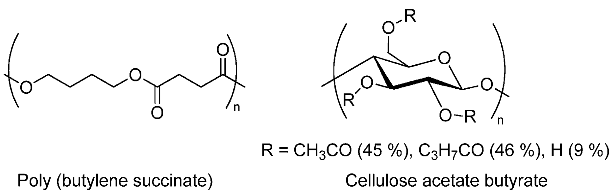

Fig. 1. Molecular structure of poly(butylene succinate) (PBS) and cellulose acetate butyrate (CAB).

the cast-blend method were transparent and elastic materials, and the Young's modulus of the CAB/PBS blend films decreased as the ratio of PBS increased to 40% because of the plasticizing effect of the PBS. On the other hand, we have used CAB as an additive derived from biomass feedstocks for PBS prepared by melt-pressing with a dry blend [16]. The strain at break was over 270% with the addition of 20% CAB, however, it seemed that the melt-pressing used as the molding method is insufficient to prepare a homogeneous blend sample.

Furthermore, the cellulose moiety of CAB is derived from biomass feedstocks, and the PBS/CAB blends become partially-biobased materials with the CAB ratio. When the product is used as a biobased material, it is important to measure the biomass carbon ratio. Recently, the accelerator mass spectroscopy (AMS) (Fig. 2) measurement method for determining the biomass carbon ratio based on the American Society for Testing and Materials (ASTM) D6866 method entitled "Standard test methods for determining the biomass carbon ratio of solid, liquid, and gaseous samples using radiocarbon analysis" has become very important in the field of biomass plastics [3,17–21]. The AMS method has been used for the carbon dating of archaeological and geological samples. In addition, the method can be applied to a mass balance study using a lower amount of ^{14}C-labelled metabolic compounds for biological systems. AMS can measure very small ^{14}C concentrations, and determine the ratio of the radiocarbon-14 to carbon-12 and 13. The ratio $^{14}C/^{12}C$ in biomass carbon is around 1×10^{-12}. Fossil resources and materials are those that contain no ^{14}C because all the ^{14}C atoms that have a 5730 year half-life time had been changed to ^{14}N during their very long burial time.

As mentioned above, the biodegradability is the most characteristic and important property of PBS. The biodegradability of a polymer blend often changes from the original polymer depending on the composition. To evaluate the biodegradability of plastics, some international standard measurement methods have been set such as the International Organization for Standard (ISO) 14851, ISO 14852, ISO 14855-1, ISO 14855-2, ISO 14853, and ISO 15985. The ISO 14855-2 as shown in Fig. 3 is the ultimate aerobic biodegradability of plastic materials under controlled compost conditions using the Microbial Oxidative Degradation Analyzer (MODA) apparatus [3,22,23].

In this paper, we mixed PBS and CAB by melt-kneading and measured its chemical properties, thermal property, and mechanical properties. The variation in the biomass carbon contents as the ratio of CAB increased and the effect of the CAB on the biodegradability of the PBS were evaluated.

2. Experimental

2.1. Materials

PBS, extended with 1,6-diisocyanatohexane (Mn = 5.0×10^5, Mw/Mn = 2.7) and CAB (Mn = 1.1×10^5, Mw/Mn = 2.8), were purchased from the Aldrich Chemical Co. All materials were used after drying at 80 °C for 24 h *in vacuo*.

2.2. Melt-kneading of PBS/CAB

PBS and CAB (ca. 10 g) were melt-kneaded using a kneading machine (Imoto Seisakusho, Co., Ltd.; Micro melt-kneader) at the rotation rate of 30 rpm and 220 °C for 15 min. The mixing part (43.0 mm length and 19.4 mm radius) is a cylinder with a rotating piston. The mixing mechanism is the Weissenberg effect generated by the surface of the piston and the melting blend resin. The mixed blends were compressed to a $100 \times 100 \times 0.5$ mm sheet at 20 MPa using a hot-pressing machine (Tester Sangyo Co., Ltd.; SA-303) at various temperatures for 5 min. After compressing, the melt-pressed films were gradually cooled to room temperature. After cooling, the sheets were cut into dumbbell-shaped specimens

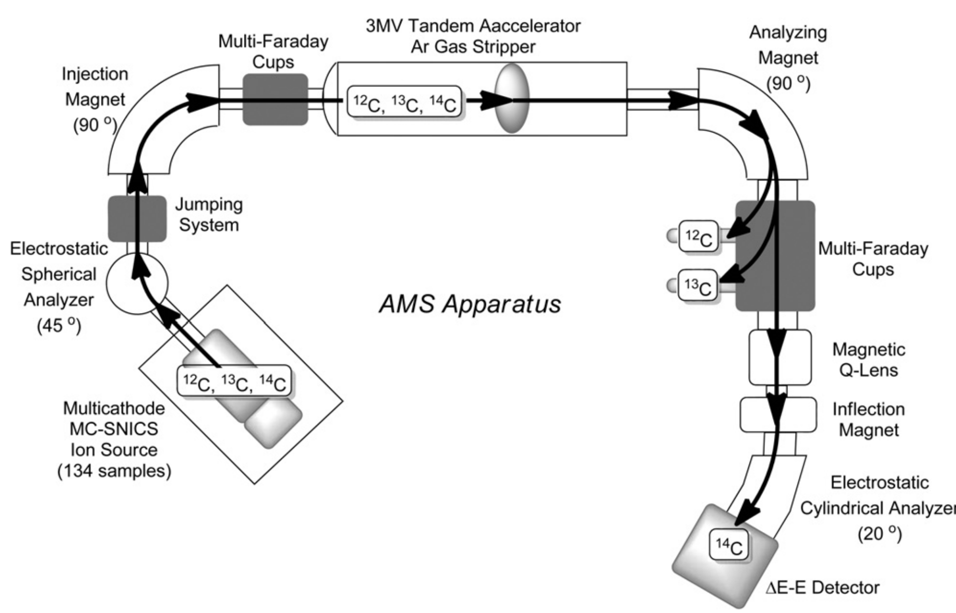

Fig. 2. Outline of the accelerator mass spectroscopy (AMS) apparatus (size ca. 15×10 m, height 2 m) for determining the percentage of modern carbon (pMC) by the ratio of $^{14}C/^{12}C$ (^{14}As) at the Institute of Accelerator Analysis, Ltd., Japan.