



BIOBASED CONTENT OF BIODEGRADABLE POLY(LACTIC ACID) COMPOSITES DIRECTLY MOLDED BY ALUMINUM TRIFLATE WITH CELLULOSE AND INORGANIC FILLERS

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Abstract

The biodegradable composites consisting of poly(lactic acid) (PLA) and particle fillers, such as cellulose, calcium carbide, kaolin and talc, were directly molded from lactide with aluminum triflate or tin 2-ethylhexanoate as a catalyst. C^{14} content in the PLA composites was measured by Accelerator Mass Spectroscopy (AMS). Biomass content of PLA composites was estimated using ^{14}C content. Mechanical properties such as, strength, modulus, strain at break, of PLA composite were investigated by compression test and tensile test. Biodegradability of PLA composites was measured by a Microbial Oxidative Degradation Analyzer (MODA). Molecular weight of PLA in PLA composites was measured by gel permeation chromatography (GPC).

1 Introduction

Recently, polymer composites are used in various industrial fields due to their good features, such as high specific modulus, high specific strength, high durability, light weight. However, a disposal of polymer composite after use remains big problem on them. One of the solutions for the above problem is a development of biodegradable composites. Biodegradable polymers and their composites directly molded from lactides with fillers were investigated in our laboratory [1-4]. Biomass, such as starch from corn and potato is focused on as a renewable resource for polymer materials instead of fossil resources. Biomass is a new carbon resource fixed from CO_2 in the modern atmosphere by photosynthesis of plants using sunlight.

Biodegradable reinforced plastics made from biomass are expected to become important materials for the commercial market. However, it is difficult for consumers to know whether a resource of polymer products is biomass or petroleum. The determination method for biomass content of plastic product is required. The degree of biomass content for plastic products including composite products is defined as the "biomass content" based on the American Society of Testing and Materials (ASTM) D6866 "Standard Test Methods for Determining the Biomass Content of Natural Range Materials Using Radiocarbon and Isotope Ratio Mass Spectrometry Analysis" [5-6].

In this study, biodegradable composite samples were directly molded from lactide polymerized by catalyst, such as, aluminum triflate and tin 2-Ethylhexanoate, with cellulose and inorganic fillers by our method [1-5]. Biomass content of composite samples was measured by Accelerator Mass Spectroscopy (AMS) based on ASTM D6866 [5-7]. The mechanical properties of samples were measured by compression test using column shape specimen. Biodegradability of samples was measured by a Microbial Oxidative Degradation Analyzer (MODA) apparatus based on ISO/DIS 14855-2 [8-10].

2 Experimental

2.1 Materials

L-Lactide (Tokyo Chemical Industry, Co. Ltd., Japan), aluminum triflate ($Al(OTf)_3$, Aldrich), tin 2-Ethylhexanoate (Wako Pure Chemical Industries,

Ltd., Japan) and glycerol (Tokyo Chemical Industry, Co. Ltd., Japan) were used as received after drying. Three kinds of cellulose particles and two kinds of inorganic particles were used as fillers for composite samples. That is, cellulose particles with different particle sizes are AVICEL (Asahi Chemical Industry Co., Ltd., Japan), and inorganic particles are calcium carbonate (Kanto Chemical Co. Inc., Japan), kaolin (Kanto Chemical Co. Inc., Japan) and talc (Wako Pure Chemical Industries, Ltd., Japan).

2.2 Sample preparation

2.2.1 Al triflate as a catalyst

PLA composites were prepared by the following procedure using Al triflate as a catalyst. L-LA and Al triflate were dried in a vacuum oven at room temperature for 12 hours. Cellulose powders were dried in a vacuum oven at 115 °C for 12 hours. L-LA (20 mM, 2.8 g), glycerol as an initiator (0.02 mM, 18.4 mg) and Al triflate as a catalyst (0.04 mM, 19.0 mg) were poured into a plastic tube in air. The plastic tube was placed in an electric oven at 100 °C. After melting of L-LA, the melting L-LA was poured into plastic tubes which were filled with particles. The plastic tubes were well mixed by a vibration. The amount of particles was varied from 0 to 1.4 g. A plastic tube was placed in an incubator at 100 °C without stirring for 6 hours. At the end of the reaction period, solid polymer composite samples were obtained in the tube after cooling to room temperature. The solid samples were removed from the plastic tubes. The filler content was calculated from the weights of the samples and fillers. Composite samples were cut into column shaped specimens for mechanical tests.

2.2.2 Tin 2-Ethylhexanoate as a catalyst

PLA composites were also prepared by the following procedure using tin 2-Ethylhexanoate as a catalyst. L-LA was dried in a vacuum oven at room temperature for 12 hours. Cellulose powders were dried in a vacuum oven at 115 °C for 12 hours. Tin 2-Ethylhexanoate (100 mg) was solved by dehydrated toluene (1 mL). L-LA with the toluene solution of catalyst was dried under reduced pressure for 40 min in order to remove toluene. A ratio of catalyst to L-LA is 0.1 mol %. After drying, the L-LA with a catalyst was heated at 110 °C and was mixed well. Then fillers were added to L-LA with a catalyst and were mixed well again. The mixture was poured into three plastic tubes heated at 110 °C. The plastic tube was placed in an electric oven at 110 °C for 48 hours. The amount of particles was

varied from 0 to 1.4 g. A plastic tube was placed in an incubator at 100 °C without stirring for 6 hours. At the end of the reaction period, solid polymer composite samples were obtained in the tube after cooling to room temperature. The solid samples were removed from the plastic tubes. The filler content was calculated from the weights of the samples and fillers. Composite samples were cut into column shaped specimens for mechanical tests.

2.3 Measurement of biomass contents of PLA composites

The sample preparation and measurements of biomass content of samples were done in the Institute of Accelerator Analysis, Ltd. (IAA), Japan based on ASTM D6866. All carbon atoms in the polymer composite samples are transferred to graphite carbons through serial oxidation and reduction reactions using quartz glass tube and a vacuum manifold system. Measuring the ration of the three carbon isotopes (^{14}C , ^{13}C and ^{12}C) by Accelerator Mass Spectroscopy (AMS) was done in IAA. Carbons in graphite transferred carbon s are accelerated by the 3MV tandem accelerator (NEC Pelletron, 9SDH-2). These measuring methods are used for dating of historical and geological samples to determine when these samples were produced and used. The percentage of modern carbon (pMC) for an oil-based carbon is 0 %. The pMC for a biomass made from fixation of CO₂ in the modern atmosphere by photosynthesis is 108 - 110 %. A measurement of a products ^{14}As ($=^{14}\text{C}/^{12}\text{C}$) content is determined relative to the modern carbon-based oxalic acid radiocarbon (Standard Reference Material (SRM) 4990c, the National Institute of Standards and Technology, NIST, USA) as a following equation. The measurement results are shown in Table.

2.4 Mechanical test of PLA composites

2.4.1 Compression test

The mechanical properties of compression tests were determined using a Shimadzu Autograph AG-10TB according to ISO 604 (JIS K 7181) with column shaped specimens with a diameter ca. 12 mm and height ca. 15 mm. Test speed was 1 mm/min. The strength and elastic modulus were investigated as the mechanical properties of samples. The strength of samples was determined as a maximum stress from the stress-strain curve. The elastic modulus was determined as a gradient of the initial linear part of stress-strain curve. The averages of strength and modulus were obtained

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using three specimens for each measurement. In addition, the specific strength and specific modulus were calculated by dividing the values of strength and modulus by density of samples.

2.4.2 Tensile test

The mechanical properties of tensile tests were determined using a Shimadzu Autograph AG-10TB according to ISO 527-3 (JIS K 7127) with dumbbell shaped specimens with a thickness 0.5 mm. Test speed was 10 mm/min. The strength and elastic modulus were investigated as the mechanical properties of samples. The strength of samples was determined as a maximum stress from the stress-strain curve. The elastic modulus was determined as a gradient of the initial linear part of stress-strain curve. The strain at break was also obtained from a stress-strain curve. The averages of above values were obtained using three specimens for each measurement. In addition, the specific strength and specific modulus were calculated by dividing the values of strength and modulus by density of samples.

2.5 Biodegradation test of PLA composites

A biodegradation test was performed using a Microbial Oxidative Degradation Analyzer (MODA) instrument (Hissan Trade Co., Ltd., Japan) in controlled compost at 58 °C based on ISO/FDIS 14855-2 [4-6]. The polymer sample powder (10 g) was well mixed in the activated compost with sea sand (ca. 400 g) and transferred to a reaction vessel. Compost with no sample was used as a blank to determine the respiration activity of this compost. Biodegradation tests were performed at 58 °C and 10 mL /min air (CO₂-free) flow rate for 45 - 90 days. The activated compost used in this study produced 50 mg CO₂ per gram of volatile solids of this compost over the first 10 days. The produced CO₂ amounts were measured once a day by measuring the weights of an absorption column for carbon dioxide and an absorption column for water. The percentage of biodegradation was calculated from the produced CO₂ amount which was cancelled respiration CO₂ amount determined from a blank, and the theoretical produced CO₂ amount of added sample. Once a week, the sample and compost were well mixed and the water content controlled.

2.6 Measurement of molecular weight of PLA composites

The molecular weight and molecular weight distribution were determined by gel permeation chromatography (GPC) using a Tosoh 8000 GPC

system with a refractive index detector. A combination of two TSK GMHXL columns (Tosoh, Japan, 7.8 mm x 30 cm) with molecular weight ranges of 1000 – 1 x 10⁷ g•mol⁻¹ was used. The columns were eluted by chloroform (flow rate of 1 mL min⁻¹ at 40 °C) and calibrated with polystyrene standards.

3 Results and Discussion

3.1 PLA composites using Al triflate as a catalyst

PLA composites using Al triflate as a catalyst were prepared according to a procedure described in 2.2.1. Properties of PLA composite samples using Al triflate as a catalyst with cellulose particles are shown in Table 1. Mechanical properties were derived by compression tests according to 2.4.1. Molecular weight was derived by GPC measurement according to 2.6. Molecular weight of composite was much less than that of PLA without cellulose particles. It is thought that the existence of cellulose particle prevent polymerization reaction of lactide monomer.

Table 1. Properties of PLA composites filled with cellulose particles using Al triflate as a catalyst

Filler content wt. %	Strength MPa	Modulus GPa	Strain at break %	Molecular weight, M_w
0	52.3	2.69	2.3	13500
20	17.7	0.80	2.0	3100

3.2 PLA composites using Tin 2-Ethylhexanoate as a catalyst

The existence of fillers made the decrease of molecular weight for PLA composite using Al triflate as a catalyst. Tin 2-Ethylhexanoate was employed as a catalyst instead of Al triflate. Properties of PLA composite samples using Tin 2-Ethylhexanoate as a catalyst with calcium carbide particles are shown in Table 2. Mechanical properties were derived by compression tests according to 2.4.1. Strength and modulus of PLA composites are less than those of PLA without fillers. Molecular weight was derived by GPC measurement according to 2.6. Molecular weight of composite was much less than that of PLA without cellulose particles. Properties of PLA composites filled with cellulose were the same tendency as those of PLA composites with calcium carbide. It is thought that

the existence of fillers prevent polymerization reaction of lactide monomer.

Table 2. Properties of PLA composites filled with calcium carbide using tin 2-ethylhexanoate

Filler content %	Strength MPa	Modulus GPa	Strain at break %	Molecular weight Mw
0	98.9	2.3	5.9	58000
20	51.4	1.3	7.9	44000
30	51.0	2.0	5.6	41000
40	46.6	1.6	4.8	31500

3.3 Biobased content measurement

Biobased contents of samples were measured according to the procedure described in 2.3. Biobased contents of PLA, PLA composites, lactide, and cellulose were determined. Biobased contents of Lactide monomer and PLA without fillers are almost 100 %. This result agrees with a fact that Lactide monomers were derived from natural plants such as corn. However, biobased content of cellulose is ca. 110 %. In 1950's, several nuclear tests have been executed and produced ^{14}C in air artificially. Biobased content is estimated by the ratio of ^{14}C in nature. The existence of artificial ^{14}C makes an error of biobased content. Cellulose may be derived from natural woods, so that the woods with long life might take the additional ^{14}C produced by the nuclear tests. It is necessary for the materials derived from woods such as cellulose to develop a calibration method of biobased content measurement.

Table 3. Properties of PLA composites filled with calcium carbide using tin 2-ethylhexanoate

Material	$\Delta^{14}\text{C}$ (%)	pMC (%)	Biobased content (%)
Lactide	90.6±4.5	109.06±0.45	101.43±0.42
Cellulose	211.8±5.3	121.18±0.53	112.70±0.49
PLA	104.6±5.2	110.46±0.52	102.73±0.48

3.4 Biodegradability of PLA composites

Biodegradability of PLA composites with cellulose were measured according to the procedure described in 2.5. For PLA using Al triflate with and without cellulose and cellulose, time at 80 % and 100 % of biodegradation of samples are shown in Table 4. PLA and PLA composite can be biodegraded faster than cellulose.

Table 4. Biodegradation time of PLA, PLA with cellulose and cellulose by ISO 14855-2

Biodegradation	80%	100%
	day	day
cellulose	44	> 90
PLA	20	37
PLA composite	27	47

4 Conclusions

Biodegradable polymer composites consisting of PLA and particle fillers, such as cellulose, calcium carbide, kaolin, talc, were prepared using Al triflate or tin 2-ethylhexanoate as a catalyst. Molecular weight of PLA composites decreases with increasing filler content. Modern carbon in the cellulose can be detected by C^{14} measurement using AMS. Estimated value of carbon in cellulose from recent natural plants is greater than 100 %. It is necessary for cellulose to develop a new estimation method of the biobased content. PLA composites were biodegraded in the compost at 58 °C for 40 days.

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