# Mechanical Properties and Biomass Carbon Ratios of Poly(butylene succinate) Composites Filled with Starch and Cellulose Filler Using Furfural as Plasticizer

**E. D. Flores,[1] M. Funabashi,[2] M. Kunioka[2]**

[1]Department of Agriculture, Bureau of Postharvest Research and Extension (BPRE), CSLU Compound, Science City of Munoz, Nueva Ecija, Philippines
[2]Research Institute for Innovation in Sustainable Chemistry, National Institute of Advanced Industrial Science and Technology (AIST), Higashi 1-1-1, Tsukuba, Ibaraki 305-8565, Japan

**ABSTRACT:** Polymer composites consisting of poly(butylene succinate) (PBS) as matrix and corn starch (CS) or cellulose filler (CF) with a small amount of furfural (FR) from biomass were prepared by a hot-pressing method at 120°C from a powder mixture. Mechanical properties of the composites' films were investigated using tensile test methods. The strain of these films was found to be developed by adding CS or CF and further improved by adding FR. The strain at break PBS with 15 wt % FR was improved by more than 16 times of that of PBS without FR. The biomass carbon ratios of polymer composites with oil-based PBS (major component) and with biobased CS, CF, and FR were evaluated by $^{14}$C concentration ratio measured by accelerator mass spectrometry (AMS) based on ASTM D6866. PBS with 40 wt % CS or CF had a biomass carbon ratio of 31 and 36%, respectively. PBS with 15 wt % FR had a biomass carbon ratio of 3.4%. This deviation was confirmed by FR content calculated from the peak area of the $^{1}$H-NMR spectrum of PBS with FR which was 3.4%, almost the same as the biomass carbon ratio measured by AMS. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 3410–3417, 2009

**Key words:** composites; mechanical properties; biodegradable; poly(butylene succinate); furfural

## INTRODUCTION

Polymer composites are widely used in industry nationwide; however, most of these are nonbiodegradable, and it is very difficult to manage their waste after use. These wastes become white pollution as a worldwide environmental problem. Development of a biodegradable polymer composite is one of the solutions to abate the aforementioned problem. Biodegradable composites can be developed by combining biodegradable matrices and biodegradable fillers.[1,2]

Poly(butylene succinate) (PBS) is one of the promising materials for the production of environmentally friendly biodegradable composites. PBS is one of the typical biodegradable polymers with the tradename "Bionolle" synthesized using polycondensation of 1,4-butanediol with succinic acid by a Japanese company[3] and has been certified as one of the biodegradable products with "Green-Pla" marks by the Japan BioPlastics Association.[4] Some applications of PBS products include packaging films for wrapping of food, office supplies, and clothing; commodity bags; industrial trays; and agricultural mulch films for covering of the soil surface in vegetable fields to protect against insects, control growing weeds, and maintain suitable environmental conditions for better growth and effective production of vegetables.[5]

Currently, PBS is an oil-based polymer. Some Japanese companies had started to synthesize PBS from biorenewable resources to reduce greenhouse gas emissions and provide sustainable alternatives to the reliance on limited petroleum-based resources.[6–8] Showa High Polymer Co.[6] and Mitsubishi Co.[7,8] are now also establishing the production of succinic acid as one of the monomers of PBS from biomass resources. Most likely in the near future, PBS will be changed to a biobased polymer by replacing its oil-based materials to half-biomass materials.

Sometimes, the mechanical properties of PBS such as softness and flexibility are insufficient for various end-use applications. For desirable mechanical properties, fillers are mixed into the biodegradable polymer matrix. Mixing a biodegradable polymer matrix with starch and cellulose filler (CF) also produces an environmentally friendly composite material. Polymer mixing with natural fillers such as starch and cellulose is considered a useful way to control biodegradability and reduce the usage of petroleum resources. Starch, a natural biodegradable polymer from renewable biomass resources, is abundant. Its

application as a filler in polymer matrix composites has been actively performed to obtain biodegradable materials at low cost.[9] Cellulose is also a natural polymer from biomass resources. Blending of a polymer matrix with CFs is also undertaken to reduce cost and improve flexibility for further processing and applications.[2] PBS composite with bamboo fiber had been produced to develop the crystallization rate of PBS during kneading process.[10] PBS nanocomposite with layered silicate was prepared by simple extrusion process.[11] These PBS nanocomposite exhibited concurrent improvements of material properties such as a melt rheology and biodegradability compared with neat PBS.

Plasticizers are also added to make the blends more flexible and processable. The plasticizer used in this study is furfural (FR), a biobased chemical compound produced from biomass resources such as agricultural and forestry waste (corn cobs, oat and rice hulls, sugarcane baggase, wood chips, etc.) by acid-catalyzed hydrolysis of polymeric pentoses followed by acid-catalyzed dehydration of aldopentoses. For crop residue feedstocks, about 10% of the mass of the original plant matter can be recovered as FR. It is used in agriculture both as a fungicide and nematicide because it is nontoxic to either humans or the environment.[12,13]

The amount of biomass carbon content in a plastic product is defined as "biobased content" according to the American Society of Testing and Materials (ASTM) D6866 "Standard Test Methods for Determining the Biobased Content of Natural Range Materials Using Radiocarbon and Isotope Ratio Mass Spectrometry Analysis" to certify and promote biomass products.[14–16] The biomass carbon ratios (biobased content) of biomaterials such as starch or cellulose are identified as 100%. However, the amount of biobased content in some compounds, such as mixture of biomass and oil-based resources or products made from unclear resources, cannot be easily determined. Biobased content can be determined from the $^{14}C$ concentration based on the ASTM D6866 standard method. In accordance with ASTM D6866, radiocarbon measurements can be performed either by using accelerator mass spectrometry (AMS), benzene synthesis, or $CO_2$ absorption. AMS is the method used for determining the biobased content of the composites in this study. In the determination of biobased content, all of the organic carbon in a sample is assumed to be either fossil or "modern" (present day) in origin. Fossil carbon (e.g., from coal or oil) is millions of years old and no longer contains any $^{14}C$. $^{14}C$ is a radioisotope with a half-life of 5730 years. Therefore, oil-based derived materials have a biobased content of 0%. On the other hand, carbon from biorenewable resources has $^{14}C$, because it has not yet undergone significant radioactive decay. $^{14}C$ atoms are continuously generated from $^{14}N$ because of the interaction with the cosmic radiation in the modern atmosphere. Therefore, the carbon found in biomass photosynthesized from $CO_2$ in the atmosphere always includes a small amount of $^{14}C$. A sample with $^{14}C$ activity that matches with that of modern carbon (MC) sources has no fossil carbon and has a biobased content of 100%. Fossil carbon combined with MC gives intermediate values for the biobased content, which is directly proportional to the amount of MC in the sample as a percentage of the total organic carbon.

In this study, the development of PBS composites was undertaken by combining PBS and corn starch (CS) or CF with FR as plasticizer. The effect of CS and CF on the mechanical properties of PBS was investigated. The effect of FR on the mechanical properties of PBS and its composites was also determined. In addition, the biomass carbon ratios of PBS composites with CS or CF and PBS with FR were measured by $^{14}C$ concentration using AMS based on ASTM D6866, and these results were compared with the carbon composition obtained using NMR analysis.

## EXPERIMENTAL SECTION

### Materials

Poly(1,4-butylene succinate), extended with 1,6 diisocyanatohexane (Aldrich Chemical Co., Japan), cellulose filler (powder form) (Avicel PH-M25, average size, 25 μm, Asahi Chemical Industry Co., Japan), corn starch (Wako Pure Chemical Industries, Japan), and furfural (Wako Pure Chemical Industries, Japan) were used as received for preparing PBS composite materials.

### Sample preparation

Poly(1,4-butylene succinate) powders for the preparation of PBS composite materials were prepared from PBS pellets as received. PBS pellets were crushed using a rotating mechanical mixer with titanium blades (10,000 rpm, 3 L) with cooling by dry ice. Crushing was done 15 times for 3 min each with a 1-min manual mixing interval to prevent overheating the motor of the mixer. After grinding, the PBS powder was dried under reduced pressure at room temperature. After drying, the crude PBS powders were fractionated by sieving through a standard and guaranteed 60-mesh sieve (250 μm). This sieve with crude PBS powders was placed on a sieve vibrator and vibrated for 15 min. The PBS powders obtained were used in the preparation of PBS composites by mixing them with CS or CF ranging from 0 to 60 wt %. PBS composites with 20 wt % of CS or CF were used in the preparation of PBS composites with varying

FR content from 1 to 30 wt %. Mixing of PBS with 0–30 wt % of FR was also prepared. After mixing, PBS composite films were prepared using the laboratory table-type test press (SA 303, Sangyo, Co., Japan). The powder mixtures were compressed with a Teflon sheet cover in a 100 mm × 100 mm × 0.5 mm stainless window frame at 20 MPa and at 120°C for 5 min. After 5 min, the melt-pressed composite films were cooled at room temperature. After cooling, the composite films were cut into dumbbell-type specimens (total length, 100 mm; total width, 25 mm; narrow width, 5 mm; thickness, 0.5 mm; effective distance between chalks, 25 mm) based on an ISO 527-type 5 (JIS K7127-3) using a dumbbell-type cutter for the tensile mechanical property tests.

### Mechanical property test

Mechanical properties such as strength and strain at break of the PBS composite films were measured using tensile tests. Tensile tests were carried out using a Shimadzu Autograph AG-1000B with dumbbell-shaped specimens at room temperature. The grip distance was 50 mm and the tensile test speed rate was 5 mm min$^{-1}$. The tensile strength at break, $\sigma_b$ (MPa), was determined as the ultimate strength required to break the materials on the stress–strain curve. Tensile strain at break, $\varepsilon_b$ (%), was determined to be the maximum strain of the stress–strain curve. An average value was taken from measurements of three samples under the same conditions for each composite film.

### Molecular weight and molecular weight distribution

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 GMH$_{XL}$ columns (Tosoh, Japan, 7.8 mm × 30 cm) with molecular weight ranges of 1000–1 × 10$^7$ g mol$^{-1}$ was used. The columns were eluted with chloroform (flow rate of 1 mL min$^{-1}$ at 40°C) and calibrated with polystyrene standards.

### Melting temperature and heat of fusion of PBS sheets

The melting temperature ($T_m$) and heat of fusion ($\Delta H_m$) were determined for pure PBS film and PBS-FR composite films with a SSC/55200 differential scanning calorimeter system (Seiko Instruments, Japan). The cut films (10 mg in an aluminum pan) were heated under a nitrogen gas flow at a rate of 10°C/min. The values of the $T_m$ and $\Delta H_m$ were calculated for the first heating scan.

### NMR analysis

The $^1$H-NMR analyses of the polyester samples were carried out on a Varian INOVA 400 (400 MHz) spectrometer. The 400 MHz $^1$H-NMR spectra were recorded at 27°C on a CDCl$_3$ solution of the polyester at a concentration of 0.01 g/cm$^3$. Tetramethylsilane (Me$_4$Si, δ 0) was used as an internal chemical shift standard.

### Measurement of biomass carbon ratio

The measurement of the ratio of the three carbon isotopes ($^{14}$C, $^{13}$C, and $^{12}$C) using AMS was performed at the Institute of Accelerator Analysis.[12] The carbon in graphite, transferred from the polymer composite samples, was ionized using a cesium cation beam. The ionized carbons were accelerated using a 3MV tandem accelerator (NEC Pelletron, 9SDH-2). Accelerated carbon isotopes were separated with an analyzing magnet by different atomic mass. $^{14}$C carbons were detected using a solid-state detector with a semiconductor absorber. The ratio of $^{14}$C to $^{12}$C ($^{14}$As) for PBS composite samples was calculated from the measured amounts of $^{14}$C and $^{12}$C.

The percentage of modern carbon (pMC) for an oil-based carbon is 0%. The pMC for biomass made by the fixation of CO$_2$ in the modern atmosphere through the photosynthesis is 108–110%. A measurement of a product's $^{14}$As ($^{14}$C/$^{12}$C) content is determined relative to the $^{14}$Ar of the MC-based oxalic acid radiocarbon (Standard Reference Material (SRM) 4990c, National Institute of Standards and Technology (NIST), USA).

## RESULTS AND DISCUSSION

### Effect of corn starch or cellulose filler on the mechanical properties of PBS composites

To develop the mechanical properties of PBS by increasing its flexibility for further processing and end-use applications, mixing of PBS with a varying content of CS (PBS/CS) or CF (PBS/CF) ranging from 0 to 60 wt % was done, and samples were prepared by a hot-pressing method.

Figure 1 shows the effect of CS and CF on the tensile strength at break of PBS composites. The strength at break of PBS/CS or PBS/CF was shown to decrease with the increasing amount of CS or CF. It was found that the development of strength was not observed for a PBS composite with CS or CF.

Figure 2 shows the effect of CS and CF on the strain at break of PBS composites. The strain at break of a PBS polymer film without any filler was 27% as shown in Figure 2. A small improvement in this strain was observed by adding CS or CF. These strains were 49 and 47% at 20 wt % content of CS or
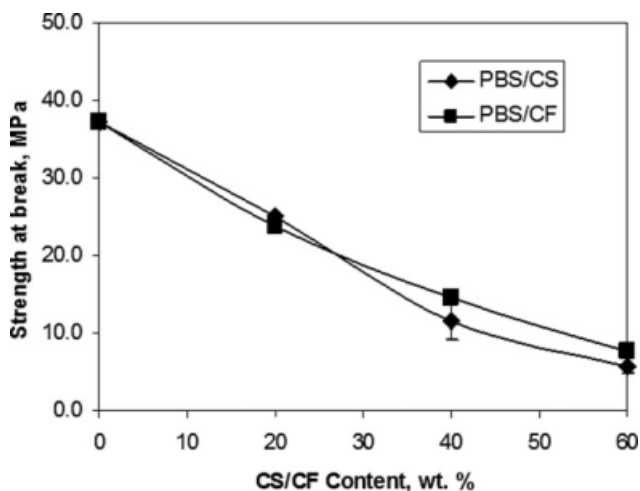
**Figure 1** Effect of corn starch (CS) or cellulose filler (CF) on the strength at break of poly(butylene succinate) (PBS)/CS and PBS/CF films hot-pressed at 120°C and 20 MPa for 5 min.

CF, respectively. In the case of CS, the strain at break of PBS composites decreased with increasing CS over 20 wt %. In the case of CF, the strains at break of the composites were maintained at over 20 wt % of CF. It was found that the strength at break of the PBS matrix was not improved by adding CS or CF; however, its strain was slightly increased. This shows that a small interaction between the PBS matrix and the powder filler was observed as a result of a small possibility of stretching especially at 20 wt % content of CS or CF.

**Effect of furfural on the mechanical properties of PBS and its composites**

With the aim of making the PBS composites more flexible and processable for a wide variety of applications, a biomass-derived additive such as FR was
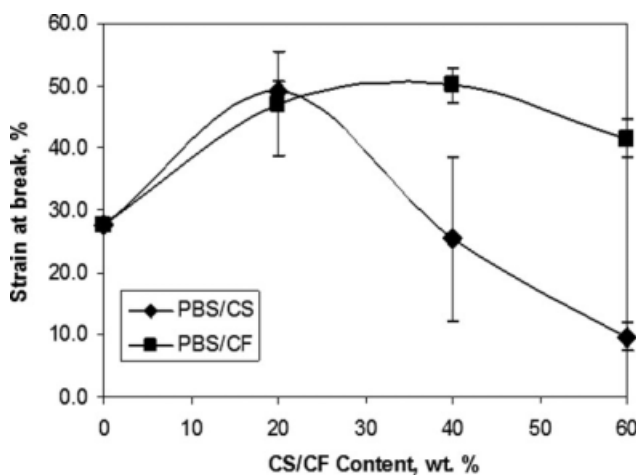


**Figure 2** Effect of CS or CF on the strain at break of PBS/CS and PBS/CF films.
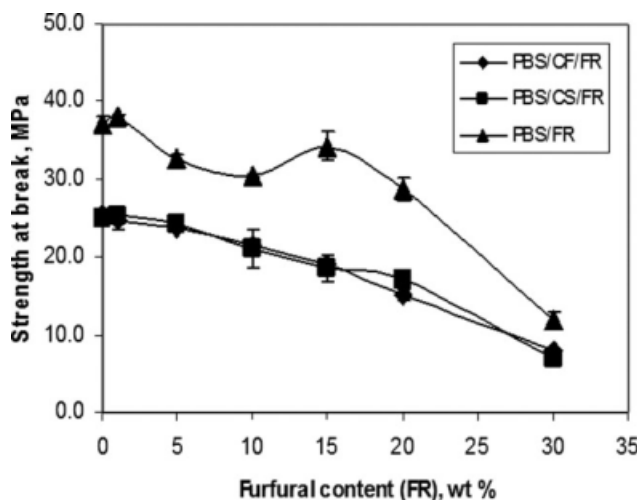


**Figure 3** Effect of furfural (FR) on the strength at break of PBS/CS/FR, PBS/CF/FR, and PBS/FR films.

used as a plasticizer. It was expected that the effect of FR as a plasticizer developed the interaction between the PBS matrix and the fillers. FR with varying content from 0 to 30 wt % was added to PBS (PBS/FR) and its composites with 20 wt % CS (PBS/CS/FR) or its composites with 20 wt % CF (PBS/CF/FR). The mechanical properties of PBS with FR and its composites with FR were measured.

The effect of FR on the strength at break of the PBS composites is shown in Figure 3. The existence of FR decreases the strength of the PBS composites. It was found that the strength at break of both PBS/CS/FR and PBS/CF/FR decreases with increasing FR content. In the case of PBS with FR (PBS/FR), the strength at break was slightly reduced by adding FR in the range of 5–20 wt % and was further reduced at 30 wt % FR content.

Figure 4 shows the effect of FR on the strain at break of PBS composites. The existence of FR causes
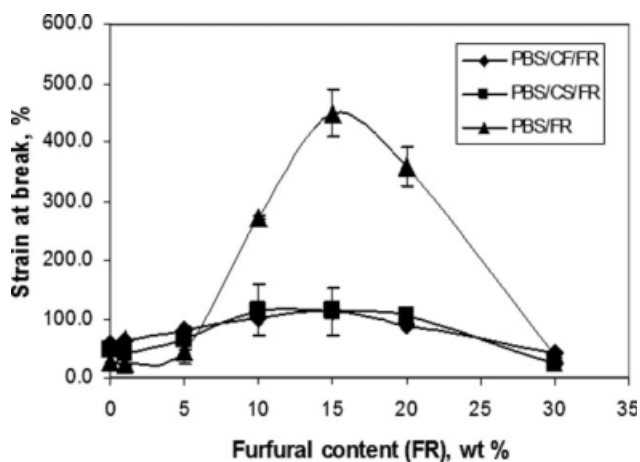


**Figure 4** Effect of FR on the strain at break of PBS/CS/FR, PBS/CF/FR, and PBS/FR films.

**TABLE I**
**Characterization of Melt-Pressed Poly(butylene succinate) (PBS) Composite Films**
**Prepared from PBS Powders and Furfural (FR) Mixture by Hot-Melting at 120°C**
**and 20 MPa for 5 min Hot-Pressing Time**

| Run | Composition[a] (wt %) | | Molecular weight[b] | | Mechanical properties[c] | |
| | PBS | FR | $M_n$ | $M_w/M_n$ | Strength at break (MPa) | Strain at break (%) |
| --- | --- | --- | --- | --- | --- | --- |
| 1 | 100 | 0 | 57,700 | 2.10 | 37.0 ± 1.0 | 27.0 ± 5.0 |
| 2 | 99 | 1 | 59,900 | 2.00 | 38.0 ± 0.5 | 23.0 ± 5.0 |
| 3 | 95 | 5 | 58,000 | 2.02 | 33.0 ± 0.5 | 46.0 ± 10.0 |
| 4 | 90 | 10 | 57,300 | 2.03 | 30.0 ± 0.2 | 273.0 ± 5.0 |
| 5 | 85 | 15 | 57,900 | 2.06 | 34.0 ± 2.0 | 450.0 ± 40.0 |
| 6 | 80 | 20 | 58,000 | 2.02 | 29.0 ± 1.5 | 359.0 ± 35.0 |
| 7 | 70 | 30 | 57,700 | 2.05 | 12.0 ± 1.0 | 38.0 ± 5.0 |

[a] Composition of powder mixtures for hot-pressing.
[b] Number-average molecular weight ($M_n$) and molecular weight distribution ($M_w/M_n$) of pure PBS film and PBS-FR composite films were determined by gel permeation chromatography (GPC).
[c] Mechanical properties of pure PBS film and PBS-FR films cut into dumbbell-shaped specimens based on ISO 527-3, type 5 (JIS K7127-3), were measured by tensile tests using a Shimadzu Autograph AG-1000B at room temperature with 5 mm min$^{-1}$ speed.

the increased of strain at break of the PBS composites. Further improvement of the strain at break of the composites was observed at 15 wt % FR content. With this amount of FR added, the strain at break of PBS composites PBS/CS/FR and PBS/CF/FR increased by four times better than the strain at break of PBS without FR from 27% to 113 and 115%, whereas PBS with FR (PBS/FR) increased by more than 16 times the strain of PBS without FR from 27 to 450%. These strains of the composites were slightly reduced at 20 wt % content and further decreased at 30 wt % FR. It was indicated that the optimal FR content for PBS composites was 15 wt %, and that beyond 20 wt % FR, the strains of the composites began to decrease.

It was found that FR in PBS composites can play a role as a plasticizer so that the strains of the PBS composites including FR were improved by more than 16 times compared with PBS without a significant reduction of its strength.

### Characterization of PBS and its composites

PBS composite samples were prepared by hot-pressing a mixture consisting of PBS and CS or CF with FR at 120°C for 5 min, as indicated previously in the Experimental section. The characterization of melt-pressed PBS composite films with FR is shown in Table I. The number-average molecular weight, $M_n$, and molecular weight distribution, $M_w/M_n$, by GPC measurements are also indicated in Table I. The $M_n$ and $M_w/M_n$ of all PBS composites with FR were about 60,000 and 2.0 the same as PBS without FR. It

was indicated that the presence of FR did not increase the molecular weight of the composites. It was confirmed that there were no possibilities of crosslinking reaction and additive reaction of FR to the PBS main chain based on no change in the $M_n$ and the FR peaks in the NMR spectrum. The FR peaks of the PBS composites with FR in the NMR spectrum as indicated in Figure 5 were not shifted from the FR used in this study.

The melting temperature ($T_m$) and heat of fusion ($\Delta H_m$) were measured using DSC for first scanning
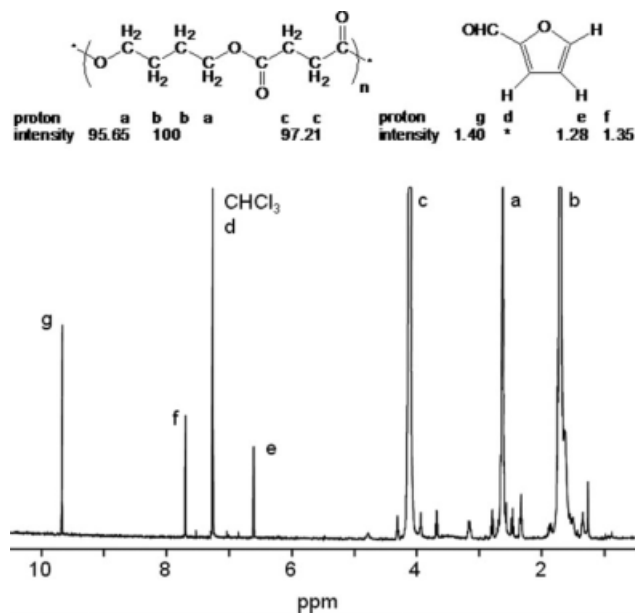


**Figure 5** $^1$H-NMR spectrum of PBS with FR (Run 5).

TABLE II
Characterization of PBS Composite Film with 15 wt % of FR Prepared by
Hot-Melting at 120°C and 20 MPa for 5 min Hot-Pressing Time

| Run | Composition[a] (wt %) | | Molecular weight[b] | | Thermal properties[c] | |
| | PBS | FR | $M_n$ | $M_w/M_n$ | $T_m$ (°C) | $\Delta H_m$ (J g$^{-1}$) |
|---|---|---|---|---|---|---|
| 1 | 100 | 0 | 57,700 | 2.10 | 114.4 | 49.8 |
| 5 | 85 | 15 | 57,900 | 2.06 | 108.9 | 61.3 |
| 5[d] | 85 | 15 | 62,200 | 2.00 | 111.2 | 93.9 |

[a] Composition of powder mixtures for hot-pressing.
[b] Number-average molecular weight ($M_n$) and molecular weight distribution ($M_w/M_n$) of pure PBS and PBS with 15 wt % of FR were determined by gel permeation chromatography(GPC).
[c] Thermal properties were measured by a differential scanning calorimeter (DSC) for first heating scanning of PBS-FR composite films at 10°C/min under nitrogen gas.
[d] This sample film was obtained from a stretched area in dumbbell-shaped samples after measuring the tensile mechanical properties.

of the obtained PBS film and the PBS/FR composite films with 15 wt % FR before and after stretching for the tensile mechanical property measurements. The $T_m$ of the obtained PBS/FR composites before and after stretching from the tensile tests was relatively the same as that of the PBS as shown in Table II. The $\Delta H_m$, however, increased from 49.8 J g$^{-1}$ for PBS to 61.3 J g$^{-1}$ for the PBS-FR composite with 15 wt % FR. By adding FR to PBS, the crystallinity of the PBS matrix was improved indicating that FR could play a role as a nucleation reagent. The $\Delta H_m$ was further increased to 93.9 J g$^{-1}$ after the film was stretched during tensile property measurements. Reorientation of the PBS molecules could proceed more smoothly with the plasticizer effect of FR during stretching in the mechanical test. It was found that the increase in $\Delta H_m$ of the stretched PBS/FR composite film confirmed the plasticizing effect of FR as indicated by the increase in the strain at break of PBS with 15 wt % of FR as mentioned previously.

### FR content and biomass carbon ratios of PBS composites determined by NMR and AMS analysis

Determination of biomass carbon ratio was an important issue in the promotion of polymer composite products developed from biorenewable resources (biomass). The biomass carbon ratios of PBS composites were determined from the $^{14}C$ concentration ratio measured using the AMS based on the ASTM D6866 standard method. Biomass carbon ratios are determined from the polymer composite powders as follows. Carbon in the polymer composite powders is oxidized to form $CO_2$ with CuO in a quartz glass tube at 500–850°C. The $CO_2$ is reduced to graphite with Fe. The $^{14}C$ concentrations, $^{14}As(^{14}C/^{12}C)$, and $^{14}Ar$, of the sample and reference material were measured for the obtained graphite using AMS ap-

paratus. Biomass carbon ratios are calculated as follows:

$$^{14}As = {}^{14}C \text{ amount (AMS counting by solid detector)} / {}^{12}C \text{ amount (AMS measuring as current) in sample} \quad (1)$$

$$^{14}Ar = {}^{14}C/{}^{12}C \text{ in reference material (NIST SRM 4990c)} \quad (2)$$

$$\Delta^{14}C = [({}^{14}As - {}^{14}Ar)/{}^{14}Ar] \times 1000 \, (\text{‰}) \quad (3)$$

$$pMC = \Delta^{14}C/10 + 100 \, (\%) \quad (4)$$

$$\text{Biomass carbon ratios} = 0.93 \times pMC \, (\%) \quad (5)$$

$\Delta^{14}C$ is the isotope differential ratio of $^{14}C$ of the sample and reference material, and pMC is the percentage of MC. MC-based oxalic acid radiocarbon [Standard Reference Material (SRM) 4990c, NIST, USA] was used as a reference material. The pMC of all biomass compounds was around 110% in 2002. The pMC can be slightly higher than 100% because of the continuing but diminishing effects of the 1950s nuclear testing programs. In this period, large amounts of $^{14}C$ were ejected into the atmosphere. Because all sample $^{14}C$ is referenced to a "prebomb" standard, all pMC values must be multiplied by 0.93 to correct for the bomb carbon and obtain the true biomass carbon ratio of the sample as indicated in eq. (5) based on ASTM D6866.

The results from the AMS and the calculated biomass carbon ratios of the PBS composites are presented in Table III. The calculated carbon ratios of CS, CF, and FR among all carbons of the PBS

TABLE III
Biomass Carbon Ratio of PBS Composite with Corn Starch (CS), Cellulose Filler (CF), or FR Calculated from $\Delta^{14}C$
Measured by Accelerated Mass Spectrometry (AMS) Based on ASTM D6866

| Run | Composition[a] (wt %) | | | | Carbon content in all carbons of PBS composite (mol %) | | | Composition[b] (C-atom%) | | $\Delta^{14}C$[c] ‰ | pMC[c] % | Biomass carbon ratio % |
|-----|-----|----|----|----|-----|-----|-----|-----|-----|-----|-----|-----|
| | PBS | CS | CF | FR | CS | CF | FR | PBS | FR | | | |
| 1 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 100 | 0 | 0 | 0 | 0 |
| 3 | 95 | 0 | 0 | 5 | 0 | 0 | 5.6 | – | – | $-978.8 \pm 0.4$ | $2.12 \pm 0.04$ | $1.97 \pm 0.04$ |
| 5 | 85 | 0 | 0 | 15 | 0 | 0 | 16.5 | 96.6 | 3.4 | $-963.3 \pm 0.5$ | $3.67 \pm 0.05$ | $3.41 \pm 0.05$ |
| 8 | 0 | 0 | 0 | 100 | 0 | 0 | 100 | 0 | 100 | $90.5 \pm 3.8$ | $109.05 \pm 0.38$ | $101.42 \pm 0.35$ |
| 9 | 60 | 40 | 0 | 0 | 34.7 | 0 | 0 | – | – | $-665.6 \pm 2.1$ | $33.44 \pm 0.21$ | $31.1 \pm 0.20$ |
| 10 | 60 | 0 | 40 | 0 | 0 | 34.7 | 0 | – | – | $-609.4 \pm 2.4$ | $39.06 \pm 0.24$ | $36.3 \pm 0.22$ |
| 11 | 0 | 100 | 0 | 0 | 100 | 0 | 0 | – | – | $66.6 \pm 4.3$ | $106.66 \pm 0.43$ | $99.19 \pm 0.40$ |
| 12 | 0 | 0 | 100 | 0 | 0 | 100 | 0 | – | – | $211.8 \pm 5.3$ | $121.18 \pm 0.53$ | $112.70 \pm 0.49$ |

[a] Composition of powder mixtures for hot-pressing.
[b] Compositions were calculated from the peak area of $^1$H-NMR spectrum of PBS with FR.
[c] Measured by AMS apparatus for graphite derived from PBS composite films, powders of CS or CF, or liquid of FR.

composite are also presented in Table III. The biomass carbon ratio of PBS, an oil-based compound was considered to be 0%. The biomass carbon ratio of CS used in this study (Run 11) was 99.19%, whereas the biomass carbon ratio of CF (Run 12) was over 112.70%. Sometimes, cellulose materials obtained from biomass resources (such as wood) grown in the 1950s, indicated higher biomass carbon ratios of more than 100% including artificial $^{14}C$ atoms from nuclear tests. To obtain accurate biomass carbon ratios, correction will be required.[13] PBS with 40 wt % CS or CF (Runs 9 and 10) had a biobased content of 31.1 and 36.3%, respectively, which are relatively the same as the calculated carbon ratio of CS (34.7%) and CF (34.7%) in all carbons of the PBS composites.

The biomass carbon ratio of FR (Run 8) based on the pMC measured by AMS was 101.41%. The PBS composite with 5 wt % FR (Run 3) and 15 wt % FR (Run 5) had biomass carbon ratios of 1.97 and 3.41%, respectively. These values obtained were lower than the carbon ratio of FR in all carbons of the PBS composite with 5.6 and 16.5 mol % calculated from the added amount of powder mixtures for film making. To clarify the amount of FR in the PBS matrix, the $^1$H-NMR spectra of FR, PBS, and PBS with FR in CDCl$_3$ were measured. Figure 5 shows the $^1$H-NMR spectrum of PBS with FR (Run 5) in CDCl$_3$. The measured carbon ratio of FR based on the peak area (1.40 at 1H(d) and 100 at 4H(b), proton position in Fig. 5) of the $^1$H-NMR spectrum of PBS with FR (Run 5) was 3.4 C-atom% ( = (1.40 × 5C/(1.40 × 5C + 25 × 8C)) × 100) and almost the same with the obtained biomass carbon ratio of 3.41% measured by AMS. A substantial amount of added FR was confirmed to be evaporated or squeezed out from PBS films during hot-pressing at 20 MPa and 120°C for 5 min. It was

found that biomass carbon ratio of PBS with 15 wt % FR was 3.41% and corresponded to the calculated carbon ratio for FR in the PBS composite film from NMR analysis.

## CONCLUSIONS

PBS composites could be prepared by hot-pressing at 120°C for 5 min. It was found that the strain at break of PBS composites was slightly improved by adding CS or CF and further improved by adding FR; especially in the case of PBS with 15 wt % FR, the strain was increased from 27% for PBS without FR to 450%. The strength of PBS was not developed by adding CS or CF. The strength of PBS with 15 wt % of FR was found to be slightly lower than PBS without FR. FR, which is derived from unused biomass such as corn cobs, could play a role as a bioplasticizer. These PBS-FR biocomposites film will be beneficial for making soft film such as a mulching film produced from all eco-friendly components. Bioplastics composites systems with biofillers and bioplasticizers will become new frontier materials in a sustainable society.

Biomass carbon ratio measurement by AMS methods was very essential to confirm the ratio of biomass in the polymer composites from the points of their reference and reliabilities in the commercial market. It was found that AMS measurement could evaluate the biomass carbon ratio for a very small amount of biomass compounds such as the PBS composite with a little FR, which was derived from biomass. The biomass carbon ratio of the PBS composites prepared in this study was very small, and the biomass carbon ratio from the AMS method corresponded to the carbon ratio of FR in the PBS composite determined by NMR analysis.

To promote biomass products effectively, the certification and a standard measuring method for the biomass carbon ratio are very important. The AMS method will be used frequently for biomass carbon ratio determination after much data collection for plastics products such as composites is done.

## References

1. Funabashi, M.; Hirose, S.; Hatakeyama, T.; Hatakeyama, H. Macromol Symp 2003, 197, 231.
2. Funabashi, M.; Kunioka, M. Macromol Symp 2005, 224, 309.
3. Fujimaki, T. Polym Degrad Stab 1998, 59, 209.
4. Japan BioPlastics Association (JBPA). Available at: http://www.jbpaweb.net/english/english.htm.
5. Vert, M. Biomacromolecules 2005, 6, 538.
6. Mizukoshi, T. Bionolle—Approach to the more environmentally-friendly green plastics, In ICTABP2; Hangzhou, China, 2006; p 123.
7. Kato, S.; Tsukuhara, T.; Kishimoto, M.; Nagaya, I. Development of green sustainable plastic (GS Pla), In ICTABP2; Hangzhou, China, 2006; p 96.
8. Shitani, N.; Kato, S. Green sustainable plastic (GS Pla) and GS Pla-degrading enzyme from fungus, In GSC-AON; Tokyo, Japan, 2007; p 235.
9. Ohkita, T.; Lee, S. H. J Appl Polym Sci 2005, 97, 1107.
10. Kori, Y.; Kitagawa, K.; Hamada, H. J Appl Polym Sci 2005, 98, 603.
11. Okamoto, K.; Ray, S. S.; Okamoto, M. J Polym Sci Part B: Polym Phys 2003, 41, 3160.
12. Martinez-Gomez, A.; Ortiz, M.; Martinez, R.; Ortiz, P.; Reguera, E. Ind Crops Prod 2004, 19, 99.
13. Zeitsch, K. J. The Chemistry and Technology of Furfural and its Many By-Products; Elsevier: Amsterdam, 2000.
14. Currie, L. A.; Klinedinst, D. B.; Burch, R.; Feltham, N. D. Nucl Instrum Methods Phys Res B 2000, 172, 281.
15. Kunioka, M.; Inuzuka, Y.; Ninomiya, F.; Funabashi, M. Macromol Biosci 2006, 6, 517.
16. Kunioka, M.; Ninomiya, F.; Funabashi, M. J Polym Environ 2007, 15, 245.