

Biodegradable Poly(butylene succinate) Blended with Biorenewable Derivatives from Polysaccharides

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Biodegradable poly(butylene succinate) (PBS) was blended with derivatives of cellulose. The amount of cellulose triacetate (CTA), cellulose propionate (CP) and cellulose acetate butyrate (CAB) were varied from 0% to 30% by weight. The PBS blends films were prepared by hot pressing method at 120 °C, 160 °C and 180 °C for 5 minutes and 10 minutes. The effects of CTA, CP and CAB on improvements in mechanical properties were investigated by measuring selected film properties such as tensile strength and elongation at break. Elongation at break increases by increasing amount of CAB and slightly increases with increasing amount of CP and hot press temperature. Elongation at break was not improved for PBS blended with CTA. The optimum elongation at break for PBS blends with CP and CAB is observed at 160 °C for 5 minutes with 20% CP and 30% CAB. The strain of PBS with CP (33.5%) and PBS with CAB (218%) was developed compared with PBS only (21%). The strength decreases with increasing amount of cellulose. It was found that the development of strength was not observed for PBS blends with CTA, CP or CAB. Thermal properties were investigated by Differential Scanning Calorimeter (DSC). In addition, biomass carbon ratios of these PBS blends were measured by accelerated mass spectrometry (AMS). The biomass carbon ratio of CAB used was about 38.55%, PBS-CAB blend had a biomass carbon ratio about 8.62%. These values were corresponded to the theoretical values for PBS-CAB blend.

Key words: Poly(butylene succinate), cellulose propionate, cellulose acetate butyrate, biodegradable polymer, biomass carbon ratio

1. INTRODUCTION

PBS has produced from petroleum commercially. PBS is a white crystalline thermoplastic with melting point of about 90–120 °C (similar to LDPE), glass transition temperature of about -45 to -10 °C (between PE and PP), tensile strength between PE and PP, and stiffness between LDPE and HDPE. PBS has excellent processing capabilities and can be processed on polyolefin processing machines at temperatures of 160–200 °C, into various products, such as injected, extruded and blown ones¹⁻². Furthermore, its raw materials, butanediol and succinic acid, may be soon available from bio-based renewable resources³⁻⁶. So that PBS will be made from biomass commercially in the near future. However, other properties of PBS, such as softness, tensile and gas barrier properties, melt viscosity for further processing and so forth, are frequently insufficient for various end-use applications. To develop the mechanical properties of PBS, blending with other bioplastics and natural fibers are studying by many researchers⁷⁻¹⁴. Kori⁷ reported the

crystallization behavior and viscoelasticity of PBS composites with bamboo-fiber. Studies about nanocomposites of PBS/clay by simple melt extrusion also have been studied and the materials properties were significantly improved than pure PBS⁸⁻⁹. Flores studied about PBS blending with natural compound such as furfural and the results showed improvement on mechanical properties and also increasing bio-based content¹⁰.

There are many unused cellulose waste from biomass. As an effective utilization of cellulose waste, the production of cellulose derivatives from those wastes will be a key issue. For example, cellulose triacetate, also known simply as triacetate, is manufactured from cellulose and acetate. Triacetate is typically used for the creation of fibres and film base. During the manufacture of triacetate the cellulose is completely acetylated whereas in regular cellulose acetate or cellulose diacetate, it is only partially acetylated. Triacetate is significantly more heat resistant

than cellulose acetate. The CTA are resistant to grease, oil aromatic hydrocarbons and most common solvents, films have hard glossy surfaces, excellent optical clarity, high dielectric constant, easily laminated, coated, folded and die-cut, cellulose acetate film prone to degradation known as Vinegar syndrome. CTA can be used as fiber or films for polarizer films for LCD projectors, specialized overhead projector transparencies, specialized photographic film, motion picture film, production of animation cels and packaging. Although CTA is not a well-biodegradable polymer originally, it could be changed to good biodegradable cellulose by the hydrolysis. Cellulose Propionate (CP) similar with the CTA is made from cellulose but the substituted groups are propionate. Cellulose Acetate Butyrate (CAB) with the butyrate groups in the cellobiose units. CTA, CP and CAB would be a biodegradable polymer in wide sense and made from biomass. Since there is a large difference in physical properties between PBS and cellulose derivatives, a material with new properties would be produced by blending these polymers.

Many kinds of resources for bioplastics products are included. Parts of these are rarely produced from petroleum. Disguise of resources that biomass products are made from petroleum with low cost to indicate those environmentally friendliness for a consumer. To improve the reliance of biomass plastics products, the measuring method of biomass carbon ratio is very important. There is the ASTM D6866¹⁵⁻¹⁶ standard that biobased content of plastics products is measured using the ¹⁴C atoms concentration to ¹²C. Because biomass carbons include very small amount of ¹⁴C and petroleum carbons include no ¹⁴C, in our laboratory the biomass carbon ratios of many kinds of bioplastics composites have been measured using accelerator mass spectrometry which can measure the ¹⁴C concentration with high accuracy to improve this ASTM standard to ISO standard by adding the data related to plastics product not included in ASTM standard.¹⁷⁻¹⁹

In this study, we investigate the mechanical / thermal properties of the PBS-CTA blends, PBS-CP blends and PBS-CAB blends in detail. In addition, the biomass carbon ratios of these PBS blends are measured using ¹⁴C concentration by accelerator mass spectroscopy.

2. EXPERIMENTAL SECTION

2.1 Materials

Poly (1,4-butylene succinate), extended with 1,6 diisocyanatohexane (PBS, Aldrich Chemical Co., Japan), Cellulose triacetate (CTA, Aldrich Chemical Co., Japan), Cellulose propionate (CP, Aldrich Chemical Co., Japan), and Cellulose acetate butyrate (CAB, Aldrich Chemical Co., Japan) were used as received for preparing PBS composite materials.

2.2 Sample preparation

PBS, CTA, CP or CAB powders for the preparation of these composite materials were prepared from these

pellets. These pellets were crushed using a rotating mechanical mixer with titanium blades (10,000 rpm, 3L) with cooling by dry ice. Crushing of PBS pellets (200 g) was done 10 times for 3 minutes each with 1 minute manual mixing interval to prevent overheating the motor of the mixer. After grinding these powders were dried under reduced pressure at room temperature. After drying the crude these powders were fractionated by sieving through a standard and guaranteed 60-mesh sieve (250 μ m). This sieve with crude these powders was placed on a sieve vibrator and vibrated for 2 x 15 minutes. And then these powders dried under vacuum pressure at 60 °C for 24 hours. These powders obtained were used in the preparation of PBS by mixing it with CTA or CP or CAB ranging from 5 to 30 wt %. After mixing, PBS blends films were prepared using the laboratory table type test press (SA 303, Sangyo, Co. Ltd, Japan). The powder mixtures were compressed with Teflon sheet cover in a 100 x 100 x 0.5 mm stainless window frame at 20 MPa using varying temperature 120 – 180 °C for 3 – 10 minutes. After time compressing, the melt-pressed composites films were cooled at room temperature. After cooling, the composite films were cut into dumb bell 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 ISO 527-type 5 (JIS K7127-3) using the dumb bell type cutter for tensile mechanical property tests.

2.3 Mechanical property test

Mechanical properties such as strength and strain at break of the PBS composite films were measured using tensile test. Tensile tests were carried out using a Shimadzu Autograph AG-1000B with a dumb bell shape 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 (MPa) was determined as the ultimate strength required to break the materials of the stress-strain curve. Tensile strain at break (%) was determined as the maximum strain of stress-strain curve. An average value was taken from measurements of three samples under the same condition for each composite film.

2.4 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 GMHXL columns (Tosoh, Japan, 7.8 mm x 30 cm) with molecular weight ranges of 1000 – 1.107⁷ g mol⁻¹ was used. The columns was eluted with chloroform (flow rate of 1 mL min⁻¹ at 40°C) and calibrated with polystyrene standards.

2.5 Melting temperature and heat of fusion of PBS sheets

The melting temperature (T_m) and heat fusion (ΔH_m) were determined for pure PBS film and PBS film blended cellulose derivatives with a SSC/55200 differential scanning calorimeter system (Seiko

Instruments Inc., Japan). The films were heated under the nitrogen gas flow at a rate of 10°C/min. The values of the T_m and ΔH_m were calculated for first heating scan.

2.6 Measurement of Biobased Contents

The measurement of the ratio of three carbon isotopes (^{14}C , ^{13}C and ^{12}C) using Accelerator Mass Spectrometry (AMS) was performed at the Institute of Accelerator Analysis (IAA, Japan). The carbon in graphite, transferred from the polymer composites 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 semi-conductor absorber. The ratio of ^{14}C to ^{12}C (^{14}As) for PBS composites 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 products ^{14}As ($^{14}\text{C}/^{12}\text{C}$) content is determined relative to the ^{14}Ar of the modern carbon-based oxalic acid radiocarbon (Standard Reference Material (SRM) 4990c, National Institute of Standards and Technology (NIST), USA).

3. RESULTS AND DISCUSSION

3.1 Effect of Cellulose triacetate, cellulose propionate or cellulose acetate butyrate 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, PBS composites with various content of cellulose derivatives were studied. Figure 1 shows the effect of CTA, CP, and CAB on the tensile strength at break of PBS blends. The strength at break of PBS blends with cellulose gradually decreases with increasing cellulose content. This may be due to poor interfacial adhesion between the PBS polymer matrix and cellulose derivatives. This is generally phenomenon in incompatible composites with different characteristics, such as hydrophobicity of the PBS polymer matrix and hydrophilicity of the cellulose derivatives. The preparation of blending films from powder mixing using hot press method is not enough for blending completely and homogeneously. However if we can get the good mechanical properties using this method, more developments for mechanical properties are expected.

Figure 2 shows the effect of CTA, CP and CAB on the strain at break of PBS blends films. The strain at break of PBS polymer film without any additives was 21% as shown in the Figure 2. Strain at break slightly decreased with increasing CTA in all blends. This may be due to the increase in the discontinuity of the PBS polymer matrix with the increase in the disperse phase. The strain at break of PBS-CP blends slightly increased with the increase of

CP content. The development of this strain was observed by adding CAB. The strain at break PBS-CAB blends increased with the increase content CAB. It indicates that the mixing situation of PBS-CAB blends is different from PBS-CTA blends and PBS-CP blends.

Figure 3 shows the effects of CAT content and conditions of press on strain at break of PBS-CTA blend samples. The strain at break decreases with increasing CTA content for any temperature. The effects of temperature and duration time of hot press were not observed significantly for these PBS-CTA blends. Almost every temperature and duration gives the same results for the same content of CTA. Figure 4 shows the effects of press conditions on strain at break of PBS-CP blend samples. The strain at break slightly increases with increasing time of hot pressing. The optimum time for hot pressing was found at 7 minutes, after that time the strain decreases. The optimum temperature of hot pressing was found at 160 °C. The minimum temperature for make the film was chosen at 120 °C because the melting point of PBS is about 120 °C. The times interpolation more than 10 minutes can gives the burns films. It could be happened because there is degradation of PBS at a high temperature for a long time. Figure 5 shows the strain of PBS-CAB blends increase with increasing time of hot pressing. The optimum time for hot pressing was found at 7 minutes for hot pressing temperature 160 °C but 5 minutes for hot pressing temperature 170 °C. The strain of PBS-CAB blend can reach 270% using 170 °C for 5 minutes hot pressing. The strength at break for PBS cellulose derivatives blends are not affected by temperature. They give almost the same results for every temperature, but slightly decreased with the increase heating time.

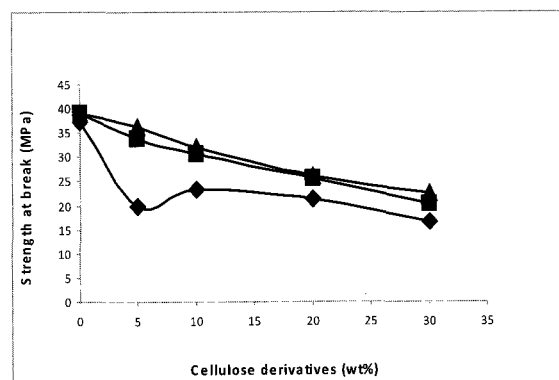


Fig.1 Effect of added amounts of cellulose triacetate (CTA), cellulose propionate (CP) or cellulose acetate butyrate (CAB) for poly(butylene succinate) (PBS) blends films to strength at break prepared by hot melt pressing at 160°C for 5 minutes. (◆) CTA, (■) CP and (▲) CAB.

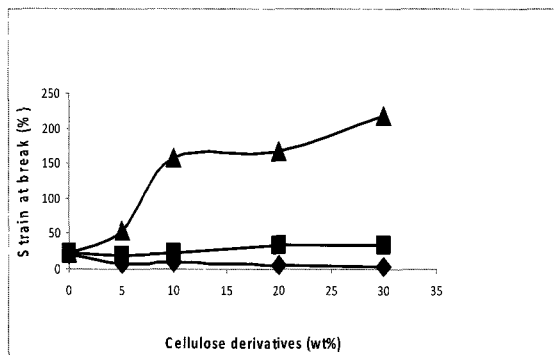


Fig. 2 Effect of added amounts of CTA, CP or CAB for PBS blends films to strength at break prepared by hot melt pressing at 160°C for 5 minutes. (♦) CTA, (■) CP and (▲) CAB.

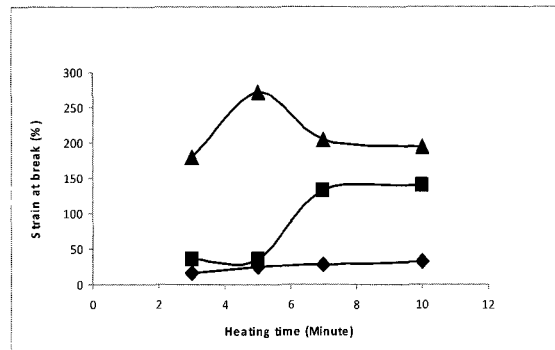


Fig. 5 Effect of temperature and time of hot pressing for the strain at break of PBS-CAB blend with 20% content of CAB (♦) 150 °C, (■) 160 °C and (▲) 170 °C.

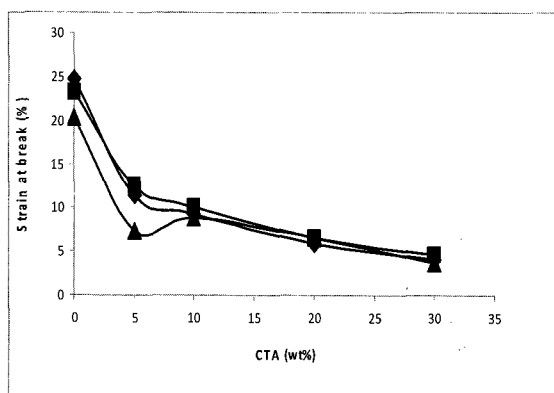


Fig.3 Effect of CTA content, temperature and time of hot pressing for the strain of PBS-CTA blend. (♦) 120 °C, 5 minutes, (■) 120 °C, 10 minutes and (▲) 160 °C, 5 minutes.

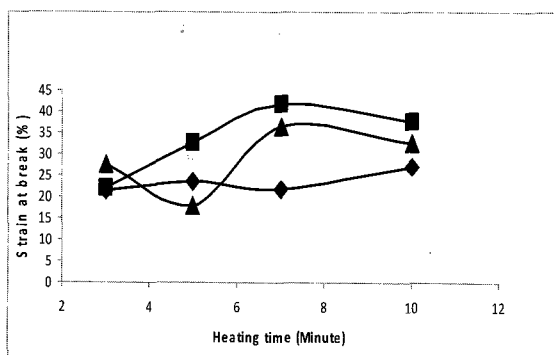


Fig.4 Effect of temperature and time of hot pressing for the strain at break of PBS-CP blend with 20% content of CP. (♦) 150 °C, (■) 160 °C and (▲) 170 °C.

In this way, PBS-CAB blends give the best result for strain at break at 170 °C for 5 minutes. The strength at break for all blends decrease by increasing the content of cellulose and slightly decreases by increasing the temperature and duration of hot pressed. The increasing of temperature and duration of hot pressed as mention above can be degraded PBS caused decreasing the strength at break.

3.2 Molecular weight

The number average molecular weight, M_n , and molecular weight distribution, M_w/M_n by GPC measurements are also indicated in Table I. It was found that M_n decreases by increasing concentration of CAB. The M_n of pure PBS films was about 61,400 whereas PBS-CAB blend with 40% CAB was about 39,500. It decreased almost 30%. The M_n of pure CAB was about 30,000, this value smaller than pure PBS thus CAB to be blended to PBS can decrease the M_n of PBS-CAB blend. As cause decreasing of M_n , the M_w/M_n increased with the increase of concentration of CAB from 2.21 for pure PBS to 2.72 for PBS-40%CAB blend.

Table I Molecular weight data of poly(butylene succinate) (PBS) blends films with cellulose acetate butyrate (CAB) using hot pressing of powder mixture at 160 °C for 5 min.

Run	Composition (wt%)		Molecular weight	
	PBS	CAB	M_n	M_w/M_n
1	100	0	61,400	2.21
2	95	5	58,200	2.22
3	90	10	54,300	2.28
4	80	20	44,200	2.53
5	70	30	38,500	2.60
6	60	40	39,500	2.72

Table II Thermal properties of PBS blends films with cellulose triacetate (CTA), cellulose propionate (CP) and CAB using hot pressing of powder mixture at 160 °C for 5 min.

Composition (wt%)				Thermal Properties	
PBS	CTA	CP	CAB	Tm (°C)	Hm (J/g)
100	0	0	0	113.3	72.6
80	20	0	0	112.5	64.0
80	0	20	0	105.7	52.6
80	0	0	20	106.3	51.1
0	100	0	0	86 ^{a)}	32.7
0	0	100	0	- ^{b)}	-
0	0	0	100	- ^{b)}	-

^{a)} Unknown peak (sample was not melt up to 120 °C.)

^{b)} There is no melting point peaks in DSC curve up to 300 °C.

Table III Biomass carbon ratio of PBS, CAB and PBS-CAB blends using hot pressing of powder mixture at 160 °C for 5 min calculated from ¹⁴C measured by AMS based on ASTM D6866

	$\Delta^{14}\text{C}$ ‰	pMC %	Biomass Carbon Ratio %
PBS	-1000	0	0
CAB	-585.5 ± 2.3	41.45 ± 0.23	38.55 ± 0.21
PBS- CAB blend	-908 ± 1.0	9.16 ± 0.10	8.52 ± 0.09

3.3 Melting temperature and heat fusion of PBS blends

The melting temperature (Tm) and heat fusion (ΔHm) were measured using DSC for first scanning of the obtained pure PBS films, PBS-CTA blends, PBS-CP blend and PBS-CAB blend. The films heated under a nitrogen gas flow at a rate 10°C/min. An endothermic peak in DSC curve of pure PBS can be seen at approximately 113 °C. This temperature corresponds to the melting point of PBS. The melting point shifted to lower temperature with addition of CTA, CP and CAB. The Tm slightly decreased from 113 °C for pure PBS to 112 – 105 °C for PBS-cellulose blends as shown in Table II. Pure CTA, CP and CAB are can't founded the Tm by DSC first scan. The ΔHm also decreased by addition of cellulose. This may be attributed to the strong interfacial interaction between PBS as polymer matrix and cellulose, confining polymer chain orientation especially CAB.

3.4 Biomass Carbon Ratio of PBS blends determined by AMS analysis

Determination of biomass carbon ratio content was an important issue in the promotion of polymer composite

product developed. The biomass carbon ratio content of PBS composites was determined from the ¹⁴C concentration ratio measured using the AMS based on ASTM D6866 standard method. Biomass carbon ratio is determined from polymer composite powders as follows. Carbon in the polymer composite powders is oxidized to form CO₂ with CuO in a quartz glass tube at 500-850°C. The CO₂ is reduced to graphite with Fe. The ¹⁴C concentration, ¹⁴As(¹⁴C/¹²C) and ¹⁴Ar, of the sample and reference material were measured for obtained graphite using AMS. Biomass carbon ratios are calculated as follows;

$$\Delta^{14}\text{C} = [({}^{14}\text{As} - {}^{14}\text{Ar}) / {}^{14}\text{Ar}] \times 1000 \quad (\%) \quad (1)$$

$$\text{pMC} = \Delta^{14}\text{C} / 10 + 100 \quad (\%) \quad (2)$$

$$\text{Biomass carbon ratio} = 0.93 \times \text{pMC} \quad (\%) \quad (3)$$

$\Delta^{14}\text{C}$ is the isotope differential ratio of ¹⁴C of the sample and reference material, and pMC is the percentage of modern carbon. Modern carbon-based oxalic acid radiocarbon [standard Reference Material (SRM) 4990c, NIST, USA] was used as a reference material. The pMC of all biobased compounds was around 110% on 2002. The pMC can be slightly higher than 100% due to the continuing but diminishing effects of the 1950s nuclear testing program. In this period large amounts of ¹⁴C were ejected into the atmosphere. Because all sample ¹⁴C are referenced to a “pre-bomb” standard, all percent modern carbon value must be multiplied by 0.93 to correct the bomb carbon and obtain a true biomass carbon ratio of the sample as indicated in equation (3) based on ASTM D6866.

The results from the AMS and calculated biomass carbon ratio content of the PBS blends were presented in Table III. The biomass carbon ratio of PBS, an oil based compound was considered to be 0% because fossil resources have no ¹⁴C and all ¹⁴C atoms with 5,730 years of half life had already changed to ¹²C under the ground after a long time. The biomass carbon ratio of CAB used was about 38.55%. The biomass carbon ratio of cellulose (C=6) is 100%. From these results, 9.56 carbon atoms of one monomer unit in CAB derived from petroleum. The biomass carbon ratio (38.55%) is calculated from the carbon atom number ratio (6/(6+9.56)). This means 1.2 of hydroxyl group in CAB monomer unit are reacted with acetic acid and 1.8 of hydroxyl group is reacted with butyric acid. In this way, the biomass carbon ratio determined by AMS can estimate the degree of substitution by alkyl groups for hydroxyl groups in cellulose units.

Theoretical carbon ratio of PBS and CAB are almost same (0.558 and 0.553). PBS-CAB blend (80/20) means 5 times dilution of biomass carbon. The biomass carbon ratio of this PBS/CAB was 8.52 % as indicated in Table I. This value was slightly higher than theoretical value (7.7 % = 38.55/5). This may be due to the elimination and evaporation of acetic and butyric acids include petroleum carbon from CAB during hot melt press blending.

4. CONCLUSION

PBS blends can be prepared by hot pressing methods at 20 MPa. It was found that strain at break of PBS blends was improved by addition of CP and CAB but not for CTA. The best result for strain at break is for PBS-20% CAB blend by 170 °C for 5 minutes of hot press methods. The strain at break can reach 270%. Otherwise the strength of PBS blends was not developed by adding derivatives of cellulose.

AMS measurement could evaluate the biomass carbon ratio for small amount of biomass compounds such as PBS blend with cellulose derivatives which was derived from biomass. PBS-CAB blend had a biomass carbon ratio about 8.62%. In the near future, we aim to increase the biomass carbon ratio also the strain and strength of PBS blended with materials derived from biomass.

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REFERENCES

- [1] T. Fujimaki, *Polymer Degradation and Stability*, **59**, 209 – 214 (1998).
- [2] X. Wang, et.al. *European Polymer Journal*, **43**, 3163 – 3170 (2007).
- [3] L. B. Schilling, *FEMS Microbiology Reviews*, **16**, Issues 2-3, 101 – 110 (1995).
- [4] S. H. Yun, et.al., *Process Biochemistry*, vol. **41**, Issue 6, 1461 – 1465 (2006).
- [5] A. Oishi, et.al., *Polymer Journal*, **38**, 710 – 715 (2006).
- [6] N. Shintani, S. Kato, *Abstract of GSC-AON2007*, 235(2007).
- [7] Y. Kori, K. Kitagawa, H. Hamada, *J. Appl. Polym. Sci.*, **98**, 603 – 612 (2005).
- [8] S. R. Suprakas, B. Mosto K. Okamoto, *Macromol. Mater. Eng.*, **290**, 759 – 768 (2005)
- [9] K. Okamoto, S. R. Suprakas, K. Okamoto, *J. Polym. Sci: Part B: Polymer Physics*, **41**, 3160 – 3172 (2003)
- [10] E. D. Flores, M. Funabashi, M. Kunioka, *J. Appl. Polym. Sci.*, (to be submitted).
- [11] F. K. Chen, et.al., *Compos. Sci. Technol.*, **66**, 2231 – 2241 (2006).
- [12] T. Uesaka, *J. Appl. Polym. Sci.*, **83**, 1750 – 1758 (2002).
- [13] T. Uesaka, *Polymer*, **41**, 8449 – 8454 (2000).
- [14] S.-H. Lee W. Siquin, *Composites: Part A*, **37**, 80 – 91 (2006).
- [15] R. Narayan, *ACS Polymer Preprint*, **46**, 319-320(2005).
- [16] ASTM D6868. Determining the biobased content of natural range materials using radiocarbon and isotope ratio mass spectrometry analysis. ASTM International 2005.
- [17] M. Kunioka, M. Inuzuka, F. Ninomiya, M. Funabashi, *Macromol. Biosci.*, **6**, 517-523(2006).
- [18] M. Kunioka, F. Ninomiya, M. Funabashi, *J. Polym. Environ.*, **15**, 281-287(2007).
- [19] M. Funabashi, F. Ninomiya, E. D. Flores, M. Kunioka, *J. Polym. Environ.*, (to be submitted).

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