

**INVESTIGATION OF POLY(LACTIC ACID) (PLA)/SUGAR BEET PULP
BIOPLASTICS: PROCESSING, MORPHOLOGY, PROPERTIES AND
FOAMING APPLICATION**

By

PENG ZHAN

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To the Faculty of Washington State University:

The members of the Committee appointed to examine the thesis of PENG ZHAN find it satisfactory and recommend that it be accepted.

Jinwen Zhang, Ph.D., Chair

Vikram Yadama, Ph.D.

Michael Wolcott, Ph.D.

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INVESTIGATION OF POLY(LACTIC ACID) (PLA)/SUGAR BEET PULP BIOPLASTICS: PROCESSING, MORPHOLOGY, PROPERTIES AND FOAMING APPLICATION

Abstract

**by Peng Zhan, M.S.
Washington State University
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Chair: Jinwen Zhang

Growing environmental problems and soaring petroleum prices have attracted intensive research interest in biopolymers. Among the commercially available options, poly(lactic acid)(PLA) exhibits excellent mechanical properties and is considered as the most promising alternative to petroleum-based polymers. However, its high price has limited adoption. In this study, sugar beet pulp (SBP), low-value residue after sugar extraction, was utilized and incorporated into PLA to reduce the cost while retaining biodegradability.

PLA and SBP were compounded with a two-step processing method. SBP was first extruded in the presence of water and glycerol as plasticizers, thereby producing a thermoplastic SBP (TSBP), which can deform like a plastic component when melted. TSBP was then compounded with PLA and extruded into a sheet. A novel compatibilizer PBAT-g-MA was found to be effective in improving interfacial adhesion of the PLA and TSBP phases. A traditional compatibilizer PLA-g-MA was compared. Due to the flexible nature of PBAT which

deterred early fracture between TSBP and PLA, composites with PBAT-g-MA exhibited better tensile properties than that compatibilized with PLA-g-MA. Improved crystallinity was also observed with PBAT-g-MA. A comparison of one-step and two-step processing methods were also developed. Results showed that the two-step processing method decreased particle size of the dispersed phase and produced better performance.

Extrusion foaming the PLA/TSBP composite was also investigated. Chemical blowing agent (CBA) content, foaming temperature and rotational screw speed significantly affected morphology and properties of resulting foam samples. Due to the low melt strength of PLA/TSBP composite, excessive amounts of CBA content resulted in early escape of the blowing agent through interconnected TSBP particles. Foaming temperature interplayed with the pressure drop and affected nucleating rate. Results showed that very fine cell structure with high cell-population density is expected in low foaming temperature. Though fast rotational screw generated a high pressure drop, which is favorable for super saturation, a shear thinning effect occurred if it went too fast.

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Abbreviation

PLA	Polly(lactic acid)
SBP	Sugar beet pulp
TSBP	Thermoplastic sugar beet pulp
PLA-g-MA	Poly (lactic acid)-g-Maleic Anhydride
PBAT-g-MA	Poly (butylene adipate-co-terphthalate)-g-Maleic Anhydrides
CBA	Chemical blowing agent
SEM	scanning Electron Microscopy
DSC	Differential Scanning Calorimetry
DMA	Dynamic Mechanical Analysis

Chapter 1 Introduction

1.1 Bio-based Plastics

Plastics play such an important role in our daily lives that you cannot go a day without seeing any plastic products, such as telephone shells, keyboards, shopping basket etc. Most of them are petroleum-based. According to a report by US Energy Information Administration, approximately 331 million barrels of liquid petroleum (LPG) and natural gas liquids (NGL) in US were consumed to make plastics product in 2006. (www.eiv.gov) According to another report by US Environmental Protection Agency, 31 million tons of plastic waste were generated in 2010, representing 12.4 percent of total Municipal Solid Waste, and that number was less than 1 percent in 1960. Also, only 8 percent of total plastic wastes were recycled in 2010. Among them, category of plastics including bags, sacks, and wraps were recycled at 12 percent. (www.epa.gov) Therefore, when we enjoy the benefits plastics bring to us, long-term environmental and energy problems are suspended to our later generations. As is known to all, petroleum is badly needed and is depleting very fast. Petroleum is not renewable, which means most of the plastics are non-renewable. Also, other problems were generated when these petroleum-based plastics are produced, for example a large amount of carbon dioxide or other chemical volatile discharged will cause ozone pollution. Finally, these petroleum-based polymers are neither biodegradable nor compostable. Plastics left in soil cannot be decomposed readily for it takes hundreds of years. Burning them causes severe pollution and the recycle rate is very low as stated before. Therefore, how can we find a way out? The answer is bio-based polymers. There are many environmental and energy benefits that bio-based plastics bring to humanity:

- a) Bio-based polymers are derived totally from renewable stock such as corn starch and vegetable oil, instead of non-renewable petroleum.
- b) Production of these polymers is green. Synthesized by fermentation means no carbon pollution into the ozone.
- c) Bio-based polymers are of course eco-friendly. They not only eliminate our concerns about the decomposition in landfill, but also save some money since recycling is no longer necessary. .

1.1.1 How biodegradation works

The organic materials biodegrade when bacteria, fungi or other microorganisms utilize their carbon substrate as sources of energy. Triggered by heat, UV light or mechanical stress, large long chain molecules are broken down into brittle fragments and were “digested” by microorganisms (aerobic or anaerobic). Under aerobic conditions, carbon sources are oxidized by microorganisms yielding carbon dioxide, water and biomass. Under anaerobic conditions, another product, methane, is produced. Methane is a greenhouse gas 25 times more potent than carbon dioxide. To compensate for this problem, people are beginning to collect methane gas to generate electricity.

1.1.2 PLA

Poly(lactic acid) (PLA) is a linear aliphatic polyester synthesized from renewable agriculture-based feed stocks, such as corn starch (in the United States), tapioca products (roots, chips or starch mostly in Asia) or sugar cane (in the rest of world) (www.wikipedia.com-1). The production of PLA causes no harm to the environment nor to human beings, so PLA is considered a sustainable alternative to petroleum-based polymers. Several major forms of PLA

exist due to the chiral nature: PLLA, PDLA and stereocomplex PLA(homo- and hetero-stereocomplexation). The synthetic procedures and structures of PLLA, PDLA, and stereoblock PLA are given in Figure 1.1. Many important properties such as degree of crystallization, mechanical strength, are strongly controlled by the ratio of L/D ratio.

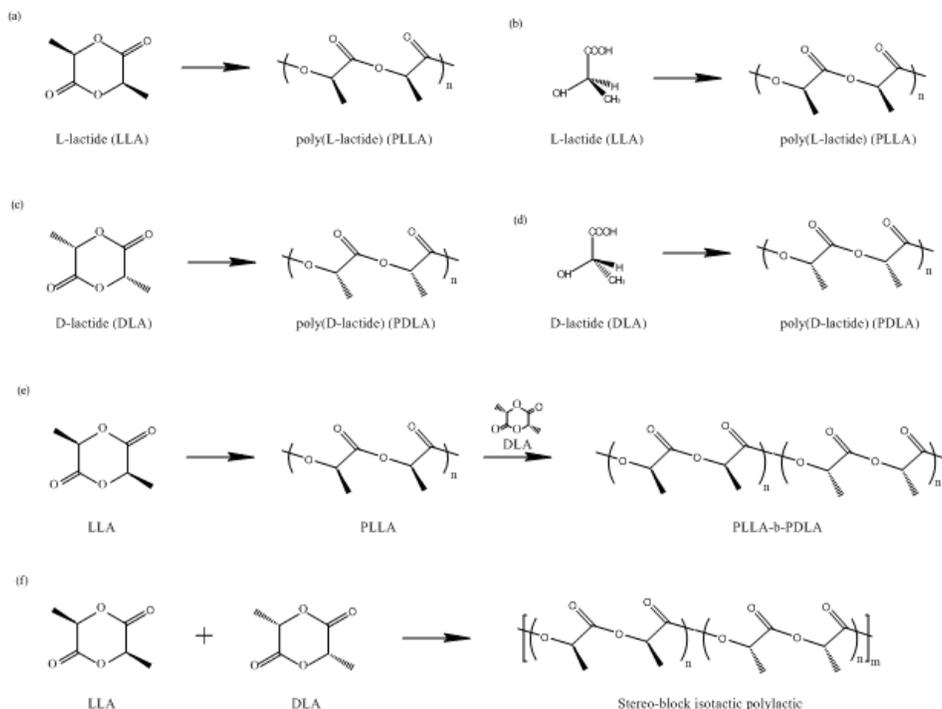


Fig. 1.1 Synthesis and molecular structures of PLLA [(a) and (b)], PDLA[(c) and (d)], and stereo-block isotactic PLA [(e) and (f)], adapted from Tsuji(Tsuji 2005).

Almost all lactic acid commercially available in the market is produced by fermentation. In 1954, DuPont patented a high-molecular weight PLA and many companies have come forward to commercialize PLA. Currently, NatureWorks LLC is the leading manufacturer of PLA in the United States. In 2001, NatureWorks LLC opened its manufacturing plant in Blair, Nebraska, USA with a capacity of 300 million pounds per year for the production of lactic acid and PLA. NatureWorks LLC has also done extensive research on the development of lactic acid based

products used for plastics or packaging applications. Other PLA manufacturers include PURAC Biomaterials in the Netherlands and several Chinese manufacturers. PURAC has been producing lactides D and L monomers for PLA production since 2009 with a capacity of several thousand tons.

Table 1.1 Material properties of PLA (adapted from (Madhavan Nampoothiri et al. 2010))

	NatureWorks PLA	Biomer L9000
Melt flow rate (g/10 min)	4.3-2.4	3-6
Density (g/cm ³)	1.25	1.25
Haze	2.2	
Yellowness index	20-60	
Tensile strength at yield (Mpa)	53	70
Elongation at yield (%)	10-100	2.4
Flexual modulus (MPa)	350-450	3600
HDT(°C)	40-45, 135	
VICAT Softening point (°C)		56
GTT (°C)	55-56	
Melting point	120-170	

Properties of PLA are largely controlled by processing temperature, length to diameter (L/D) ratio, annealing time and molecular weight. PLA has gained its application in packaging, textiles, fishing and even biomedical areas, due to its transparency, high modulus (3 GPa), high strength (50-70 MPa), biodegradability, and commercial availability. Table 1.1 summarizes some of the

properties of PLA. Processing methods of PLA include inject-molding, extrusion, blow molding, casting, foaming, blending, fiber spinning, and compounding (Lim et al. 2008).

1.1.3 Sugar beet pulp

Currently, sugar beet is grown across the world as a commercial crop to produce sugar. Around 30% of the world's total sugar supply comes from sugar beets. The first successful attempt to produce sugar beet in United States can be traced to the 1870s. In 1990, about 1,400,000 acres of 14 states has been growing sugar beets (www.purdue.edu). In 2010, 227.7 million metric tons of sugar beets were produced in the world. (www.wikipedia.com-2) USA, following France, is the second leading producer which accounts for about 12% of total production in 2009. (www.wikipedia.com-2)

Sugar beet pulp (SBP) is the byproduct of sugar extraction. Typically, 100 g of sugar beet pulp contains 8 g protein, 5.5 g carbohydrate, 67 g polysaccharide (42% hemicellulose, 28% cellulose, 27% pectin and 3% lignin), as well as about 5 g of minerals and fat. Currently, SBP is either used as low value animal feed or simply disposed of as solid waste which may cause additional cost. In recent years, intense research has been done to search for value-added applications of SBP. Ingredients have been extracted from raw SBP and utilized, such as cellulose fibrils (Dufresne et al. 1997) (Leitner et al. 2007), pectin and alkaline soluble polysaccharides (Turquois et al. 1999) (Oosterveld et al. 2001) (Kuuva et al. 2003). SBP as a whole has also been used as reinforcing filler or thermoplastic to blend with other polymers, such as PLA (Finkenstadt et al. 2007) (Finkenstadt et al. 2008) and PBAT (Liu et al. 2011).

1.2 Extrusion foaming

1.2.1 Nucleation, growth and solidification in extrusion foaming

Foam products are used every day and everywhere mainly as packaging material for protecting objects during transportation from household to industrial use. Generally, a foaming process includes the following four stages, namely, dissolution of foaming agent, bubble nucleation, bubble growth, and stabilization (Lee and Ramesh 2004). Any gas can serve as a blowing agent, but its solubility, diffusivity and volatility can significantly affect some of the main properties of a foam product.

In continuous foaming extrusion, processing pressure must be kept higher than the vapor pressure of the polymer melt/gas to ensure one phase homogeneity of the polymer melt/blowing agent. As the polymer melt flows out of the die, a sudden pressure drop satisfies the super-saturation criteria. Nucleation is believed to occur when:

$$P_s = P_q \quad (1).$$

$P_s = P_q$ where P_s represents the system pressure, P_{eq} is equilibrium pressure (Lee et al. 2007). It is worth to note that the fluctuation of pressure and uneven distribution of heat induced by high shear stress in extrusion foaming renders it more complex than batch foaming.

After nucleation, the whole system is still in super-saturation. Gas diffuses into bubbles and expands the bubbles. Bubble expansion lowers the gas concentration which facilitates the gas diffusion again and eventually equilibrium will be achieved. In general, the subtle criteria for bubble growth is:

$$P_{ce} > P_b > P_{me} \quad (2).$$

where P_{ce} is pressure induced by gas diffusion, P_b is bubble pressure, P_{me} is pressure of vicious media, subtitle ce and me stand for chemical and mechanical, respectively (Lee et al. 2007). In low viscous media, bubbles expand easily and gas diffusion rate is relatively low. It is so called chemically controlled growth. In high viscous media, low expansion rate renders it mechanically controlled growth. Generally, the differences of these pressures serve as the main driving force for cell growth.

It is already known that polymers are a viscoelastic material and its viscosity is temperature dependent. Cooling from molten state to solid state is a thermal process and also the main mechanism of increasing the viscosity and strength of polymer so as to stop bubble expansion and freeze the cellular structure.

1.2.2 Biodegradable foams

Interest in biodegradable foams is growing in recent years due to the high price of petroleum and landfill waste concerns associated with synthesized polymers. Foam products containing PLA (Di et al. 2005) (Ema et al. 2006) (Lee et al. 2008), PBAT (Stagner and Narayan 2011), soy protein (Liu et al. 2011), starch (Glenn and Orts 2001), cellular fiber (Kuboki et al. 2009), wood flour (Matuana and Mengeloglu 2002) are reported. In our work, sugar beet pulp and a PLA biodegradable composite was first developed into foam. (Lee et al. 2007) outlined that biodegradable foaming and conventional thermoplastic foaming are different as follows:

- a) Polymers from biodegradable foaming are based on natural resources whereas thermoplastic foams are petroleum-based.
- b) Biodegradable foams are water soluble, degradable, and water sensitive whereas thermoplastic foams exhibits good water resistance and non-degradable.

- c) Foaming process for biodegradable foams must have low shear whereas foaming process for thermoplastic is relatively flexible and broad.
- d) Microcellular foam sheet for biodegradable plastics is difficult to achieve due to corrugation and equipment issues.

1.3 Problem Statement

The properties of PLA are comparable with that of some of the mainstream petroleum-based plastics, but the price of PLA is still relatively high. Sugar beet pulp is of very low cost. PLA and SBP are complimentary to each other when blended. However, the following aspects have to be considered:

- a) PLA is hydrophobic whereas SBP is hydrophilic. Strong compatibilization is necessary for blending PLA and SBP. Previous study from our group shows that pMDI proves to be a good compatibilizer for PLA and SBP filler, but it is uncertain if pMDI is also suitable for thermoplastic-like SBP (TSBP). This uncertainty is because water, which is a plasticizer for SBP to TSBP, can also react with pMDI;
- b) The addition of SBP to PLA will increase melt viscosity of the blend so that processability is harmed. Increasing the extrusion temperature is a good way to improve processability, but SBP in the extruder barrel may thermally degrade, especially when residence time is long;
- c) Both PLA and SBP are brittle, so increasing impact strength of the composite remains in question.

- d) PLA exhibits low heat resistance, because of its low crystallinity and relatively low glass transition temperature ($\sim 60^{\circ}\text{C}$). Therefore, heat distortion temperature (HDT) is very low.
- e) Though PLA exhibits very good mechanical properties, its price is still relatively high compared to other petroleum-based polymers.
- f) Density of PLA is relatively high ($1.2\sim 1.3\text{ g/cm}^{-3}$) compared to other polymers in common use such as HDPE ($0.92\sim 0.98\text{ g/cm}^{-3}$), PP ($0.85\sim 0.91\text{ g/cm}^{-3}$), or ABS ($1.03\sim 1.08\text{ g/cm}^{-3}$).
- g) Although SBP has a nucleating effect during cell formation, immiscibility and uneven distribution of SBP in the PLA phase makes it hard to develop a foam product with very fine cells.

1.4 Research Objectives

PLA is a biodegradable polyester synthesized by the ring-opening polymerization of lactides. Lactide is the cyclic dimer of lactic acid which is produced by the fermentation of corn starch feedstock. PLA provides a potential alternative to petroleum-based polymers in many applications partially because of its high strength and stiffness, but its price is relatively high. SBP, the residue of sugar extraction, is merely used as low value animal feed or disposed of as landfill waste. PLA and SBP are complementary with each other. SBP can lower the cost of PLA and may increase HDT with the basic premise of biodegradability. PLA provides an excellent matrix for SBP because PLA exhibited good processibility (injection and extrusion) and increases the water resistance of SBP.

SBP can be melt processed like a thermoplastic with the existence of an extra plasticizer, i.e. water and glycerol, to form thermoplastic SBP (TSBP) (Liu et al. 2011). Both TSBP (two-step method) and dried SBP (one-step method) with plasticizers can be compounded with PLA. When SBP is blended with PLA, the morphology of SBP is largely controlled by (not limited to) total water/glycerol content and its ratio, compatibilizer type and content, one-step/two-step processing, hence the properties are manipulated in many ways.

SBP is highly hydrophilic whereas PLA is hydrophobic. It is of great interest to investigate the compatibilization of PLA and SBP to achieve better performance of the composite. Chen et al. (Chen et al. 2008) studied the effect of dried SBP (as filler) in the PLA matrix using pMDI as the compatibilizer. Mechanical properties and water resistance were greatly improved, indicating the establishment of good compatibilization. However, when TSBP is blended with PLA, the residue water will react with pMDI and the compatibilization is compromised. For the blends of PLA and TSBP, we choose PLA-g-MA and PBAT-g-MA as compatibilizers.

Aims of this study include:

- a) Investigate and compare effects of PLA-g-MA and PBAT-g-MA as compatibilizers on tensile, thermal, morphology properties of PLA/TSBP composites.

Traditionally, the maleic anhydride (MA) grafted polymer is used as a reactive compatibilizer for natural polymer composites with that polymer. Therefore, PLA-g-MA is expected to concentrate at the interface between PLA and SBP and the anhydride groups of the grafted PLA and hydroxyls of natural polymer form covalent bonds, resulting in effective compatibilizer in the PLA/natural fiber system. On the other hand, because PBAT can significantly improve tensile toughness and ductility

of the PLA matrix, use of PBAT-g-MA as a compatibilizer may also introduce improved tensile toughness and ductility to the PLA/SBP composites.

- b) Compare one-step and two-step processing methods.

One-step processing refers to a single process in which plasticization of SBP and blending with PLA took at the same time. The cell wall is broken by high shear stress and water-soluble pectin is released in the presence of water. On the other hand, sugar beet pulp (SBP) alone can be turned into a thermoplastic-like matter (TSBP) using a method very similar to that of preparing thermoplastic starch (TPS). The resulting TSBP can then be blended with PLA. This is the so-called two-step processing method. In this case, most of the plasticizers are considered to remain in the TSBP phase. Therefore, TSBP may have better deformability than SBP using the one-step processing method and thus influence resulting properties.

- c) Develop extrusion foaming of PLA/TSBP composite.

The resulting foam properties such as bulk density and cell density are highly manipulated by the chemical blowing agent content, foaming temperature and rotational speed.

Reference

- Chen, F., L. Liu, et al. (2008). "Performance Enhancement of Poly(lactic acid) and Sugar Beet Pulp Composites by Improving Interfacial Adhesion and Penetration." Industrial & Engineering Chemistry Research **47**(22): 8667-8675.
- Di, Y., S. Iannace, et al. (2005). "Reactively modified poly (lactic acid): Properties and foam processing." Macromolecular Materials and Engineering **290**(11): 1083-1090.
- Dufresne, A., J. Y. Cavaille, et al. (1997). "Mechanical behavior of sheets prepared from sugar beet cellulose microfibrils." Journal of applied polymer science **64**(6): 1185-1194.
- Ema, Y., M. Ikeya, et al. (2006). "Foam processing and cellular structure of polylactide-based nanocomposites." Polymer **47**(15): 5350-5359.
- Finkenstadt, V., C. K. Liu, et al. (2008). "Mechanical property characterization of plasticized sugar beet pulp and poly (lactic acid) green composites using acoustic emission and confocal microscopy." Journal of Polymers and the Environment **16**(1): 19-26.
- Finkenstadt, V. L., L. S. Liu, et al. (2007). "Evaluation of poly (lactic acid) and sugar beet pulp green composites." Journal of Polymers and the Environment **15**(1): 1-6.
- Glenn, G. and W. Orts (2001). "Properties of starch-based foam formed by compression/explosion processing." Industrial crops and Products **13**(2): 135-143.
- Kuboki, T., Y. H. Lee, et al. (2009). "Mechanical properties and foaming behavior of cellulose fiber reinforced high-density polyethylene composites." Polymer Engineering & Science **49**(11): 2179-2188.
- Kuuva, T., R. Lantto, et al. (2003). "Rheological properties of laccase-induced sugar beet pectin gels." Food Hydrocolloids **17**(5): 679-684.
- Lee, S., L. Kareko, et al. (2008). "Study of thermoplastic PLA foam extrusion." Journal of Cellular Plastics **44**(4): 293-305.
- Lee, S. T., C. B. Park, et al. (2007). Polymeric foams: science and technology, CRC.

- Lee, S. T. and N. S. Ramesh (2004). Polymeric foams: mechanisms and materials, CRC.
- Leitner, J., B. Hinterstoisser, et al. (2007). "Sugar beet cellulose nanofibril-reinforced composites." Cellulose **14**(5): 419-425.
- Lim, L. T., R. Auras, et al. (2008). "Processing technologies for poly(lactic acid)." Progress in Polymer Science **33**(8): 820-852.
- Liu, B., S. Bhaladhare, et al. (2011). "Morphology and Properties of Thermoplastic Sugar Beet Pulp and Poly(butylene adipate-co-terephthalate) Blends." Industrial & Engineering Chemistry Research.
- Liu, B., L. Jiang, et al. (2011). "Extrusion Foaming of Poly (lactic acid)/Soy Protein Concentrate Blends." Macromolecular Materials and Engineering **296**(9): 835-842.
- Liu, B., J. Zhang, et al. (2011). "Preparation and Properties of Water and Glycerol-plasticized Sugar Beet Pulp Plastics." Journal of Polymers and the Environment **19**(3): 559-567.
- Madhavan Nampoothiri, K., N. R. Nair, et al. (2010). "An overview of the recent developments in polylactide (PLA) research." Bioresource technology **101**(22): 8493-8501.
- Matuana, L. M. and F. Mengelöglu (2002). "Manufacture of rigid PVC/wood-flour composite foams using moisture contained in wood as foaming agent." Journal of Vinyl and Additive Technology **8**(4): 264-270.
- Oosterveld, A., I. Pol, et al. (2001). "Isolation of feruloylated arabinans and rhamnogalacturonans from sugar beet pulp and their gel forming ability by oxidative cross-linking." Carbohydrate polymers **44**(1): 9-17.
- Stagner, J. and R. Narayan (2011). "Preparation and Properties of Biodegradable Foams." Journal of Polymers and the Environment: 1-9.
- Tsuji, H. (2005). "Poly(lactide) Stereocomplexes: Formation, Structure, Properties, Degradation, and Applications." Macromolecular Bioscience **5**(7): 569-597.

Turquois, T., M. Rinaudo, et al. (1999). "Extraction of highly gelling pectic substances from sugar beet pulp and potato pulp: influence of extrinsic parameters on their gelling properties." Food Hydrocolloids **13**(3): 255-262.

www.eiv.gov. Retrieved April 2012, from <http://www.eia.gov/tools/faqs/faq.cfm?id=34&t=6>.

www.epa.gov. Retrieved May 2012, from
<http://www.epa.gov/wastes/conservation/materials/plastics.htm>.

www.purdue.edu. Retrieved May 2012, from
<http://www.hort.purdue.edu/newcrop/afcm/sugarbeet.html>.

www.wikipedia.com-1. Retrieved May 2012, from
http://en.wikipedia.org/wiki/Polylactic_acid.

www.wikipedia.com-2. Retrieved May 2012, from http://en.wikipedia.org/wiki/Sugar_beet.

Chapter 2 Compatibilizer effects on Morphology and Properties of Extruded Sugar Beet Pulp and Poly(lactic acid) Composite Sheets

ABSTRACT

In this study, thermoplastic-like sugar beet pulp (TSBP) was prepared first in the presence of water and glycerol. TSBP (40 parts) was then compounded with PLA (60 parts) and finally extruded into sheets by twin screw extrusion. Effects of PLA-g-MA and PBAT-g-MA as compatibilizers and their contents were compared. Wettability was greatly improved with the addition of compatibilizers. One step PLA/SBP composites were also prepared as controls to compare with PLA/TSBP composites. Results showed that two-step PLA/TSBP composite exhibited better mechanical properties and smaller particle size. The dynamic mechanical property was also studied to examine the compatibilizer effect. It is interesting to note that the addition of PBAT-g-MA increased cold crystallization when the DSC curves were generated.

Keywords: *PLA, sugar beet pulp, compatibilizer*

2.1 Introduction

In recent years, due to the drawbacks of petroleum-based polymers, such as depleted stock, environmental problems induced by both disposal and production process as well as potential health problem caused by food packaging (Chen 2010), biodegradable polymers are gaining more and more attention. Poly(lactic acid) (PLA), a commercially available thermoplastic polyester, is derived from renewable feedstock by fermentation of corn starch. PLA is universally accepted as compostable and exhibits mechanical properties comparable to those of petroleum-based polymers (Garlotta 2001). These advantages help PLA gain broad application, such as tissue engineering, drug delivery, disposable plastic bags, and thermal foamed products.

However, the positive impact of PLA has been severely compromised by its low heat distortion temperature (HDT), lower rate of biodegradation, unsatisfactory toughness and high cost (Chen et al. 2008) (Liu et al. 2010). Therefore, to overcome these drawbacks and/or improve some particular properties, PLA has been blended with both plastics and fillers, for example, starch (Manjula Dilkushi Silva et al. 2011), soy protein (Zhang et al. 2006) (Liu et al. 2010), sugar beet (Chen et al. 2008), PBAT (Jiang et al. 2006) (Jiang et al. 2007), wood fiber (Huda et al. 2006), etc. Liu (Liu et al. 2010) investigated PLA/EBA-GMA/EMAA-Zn ternary blend with super-toughness. The incorporation of natural fibers is generally believed to result in high modulus and lower cost. Liu (Liu et al. 2010) studied PLA/soy protein composites with dual compatibilizers effect, and obvious increased mechanical properties compared to neat PLA was shown. Chen et al. (Chen et al. 2008) reported dried sugar beet pulp/ PLA blends with comparable tensile properties with neat PLA (Liu et al. 2011).

Sugar beet pulp (SBP), the residual from sugar extraction, is mainly used as feed stock or disposed of as solid waste. It makes up of three kinds of polysaccharides: namely, pectin, cellulose and hemi-cellulose, which are in approximately equal amount, and they make about 80wt% of the total mass. Other ingredients include proteins, lignin, residual sugar and moisture. Cell wall of SBP can be broken by chemical methods, enzyme or very high shear stress (Rouilly et al. 2006) and valuable target ingredient are released and can be separated. Dufresne (Dufresne et al. 1997) extracted cellulose fibrils and casted them into sheet. He studied its mechanical properties and found that pectin served as a binder and improved stress transfer ability. Leitner (Leitner et al. 2007) also separated cellulose fibrils and incorporated them into polyvinylalcohol and phenol-formaldehyde as nanofibril-reinforcement. Also, extraction and utilization of pectin and alkaline soluble polysaccharides has been reported (Turquois et al. 1999) (Oosterveld et al. 2001) (Kuuva et al. 2003). However, utilization of intact SBP has also been reported. SBP can be processed alone as a plastic (Rouilly et al. 2006) (Rouilly et al. 2006) (Rouilly et al. 2009) (Liu et al. 2011) or blended with other polymer matrix, such as PLA (Liu et al. 2005) (Finkenstadt et al. 2007) (Chen et al. 2008) (Finkenstadt et al. 2008) and PBAT (Liu et al. 2011). Dried SBP can be turned into thermoplastic SBP(TSBP) with existence of water, glycerol and/or sorbitol(Finkenstadt et al. 2008) as plasticizers by extrusion. Liu et al. (Liu et al. 2011) studied neat TSBP sheets and found that melt processing ability and mechanical properties greatly depended on its water content, but that neat TSBP exhibited very low strength and water resistance. Besides, large amount of plasticizers (50%) were used which added expense. Finkenstadt et al. (Finkenstadt et al. 2008) investigated the plasticizer effect on TSBP/PLA composites and found that the addition of plasticizers reduced modulus and strength but increased elongation. Polymeric diphenylmethane diisocyanate (pMDI), which was originally an

effective coupling agent for wood plastic composite (Zhang et al. 2004), was also found to be effectively in dried SBP/PLA system. (Chen et al. 2008). The results showed very good mechanical properties. With addition of 2 wt% of pMDI, modulus of the PLA/SBP composite was 32% higher than that of neat PLA. However, moisture content in TSBP may compromise pMDI compatibilization (Liu et al. 2010). The maleic anhydride (MA) group is highly reactive with the hydroxyl and amino group, so MA grafted PLA has widely been used to improve interfacial bonding between PLA/nature polymer composites, such as starch (Zhang and Sun 2004) (Huneault and Li 2007) and soy protein (Zhu et al. 2012). PBAT was found to be a good toughening modifier for the PLA matrix, (Jiang et al. 2006) therefore MA grafted PBAT (PBAT-g-MA) was expected to improve both the PLA matrix and interfacial adhesion.

In this work, the effects of MA grafted type compatibilizers (PLA-g-MA and PBAT-g-MA) on PLA/TSBP composite sheet are discussed. SBP was turned into TSBP using a twin screw extruder and was blended with PLA and finally extruded into sheets. SBP was also compounded with PLA as control. This study aims at 1) comparing effects of PLA-g-MA and PBAT-g-MA compatibilizers and; 2) comparing one-step and two-step processing method. The content of compatibilizer varied from 0 to 5 wt% on the total weight of PLA and dry SBP. Water and glycerol were maintained at 20 wt% on the basis of dry SBP. The resulting sheet samples were characterized with tensile test, DMA, SEM and DSC.

2.2 Experimental

Materials. PLA (4042D) was employed in this study and obtained from NaturalWorks. SBP (Fibrex 600), obtained from Nordic Sugar Company, exhibits a particle size of less than 0.5 mm. Every 100 g of such SBP is composed of approximately 67 g Fibre (42% Hemicellulose, 28%

Cellulose, 27% Pectin and 3% Lignin), 8 g Protein, 5.5 g Carbohydrate, 5.5 g Sugar, 1 g fat, 4 g Minerals and roughly 6g moisture. Anhydrous glycerol was obtained from J.T. Baker. All the materials above are used as received without any further purification. MA grafted PBAT and MA grafted PLA were prepared by ourselves, using reactive extrusion method. Grafting degree was determined according to a titration method. It was 1.18% for PBAT-g-MA and 0.75 for PLA-g-MA.

Preparation of TSBP. According to a study from our group, both water and glycerol are effective plasticizers. In this work, water (20 parts) and glycerol (20 parts) were slowly added to SBP (100 parts, dry weight) while mixing by a kitchen mixer for at least 5 minutes. The formulated SBP were sealed in a plastic bag and equilibrated at room temperature overnight. After equilibration, SBP was compounded using a co-rotating twin extruder (Leistritz ZSE-18HP) equipped with a volumetric feeder. The diameter of each screw is 17.8 and length over diameter ratio (L/D) is 40. Feed throat zone was cooled by running tap water to keep the water from evaporating before compounding. The extruder also has 7 heating zones and an adaptor/die section which is also temperature-controlled. All the temperatures were set as 85 °C and no die was equipped.

Compounding of TSBP/PLA composites. The two-step method in which plasticization of SBP and compounding with PLA were processed separately was primarily employed in this work in order to minimize the particle size of SBP and obtain TSBP/PLA composite sheets with smooth surfaces. TSBP (40 parts, dry weight), PLA (60 parts) and varying loadings (1, 3, 5 parts) of compatibilizers (PLA-g-MA and PBAT-g-MA) were sealed in the plastic bag and mixed by hand shaking. TSBP and PLA were then compounded by the same extruder mentioned above with a temperature profile of 120, 140, 160, 170, 170, 160, 160, 150 °C from inlet to outlet

followed by pelletization. The extruder was vented at the sixth heating zone and equipped with a two-hole strand die. Screw speed was maintained at 100 rpm. Pelletized composites were dried at 80 °C for 12 h to remove the water, because water can lead to hydrolysis of PLA and water vapor during processing will cause surface defect on the sheet.

Preparation of TSBP/PLA composite sheets. Dried pellets were extruded with the same extruder equipped with a 40 mm wide, 2 mm thick sheet die. Temperature profile was set as 110, 130, 150, 160, 150, 150, 135, 130, 130 °C and rotation speed was also maintained as 100 rpm. The extruded sheet was drawn by a floor-standing two-roll haul off system (Thermo Fisher Scientific, England). Temperature was set as 70 °C.

Formulation. Table 2.1 listed all the formulations. Compatibilized samples were simply denoted by the name of compatibilizers and followed by the content. For example, formulation of PLA-g-MA-1 contains 1 wt% of PLA-g-MA. Uncompatibilized is the sample without compatibilizers. One-step processing method is denoted as “one-step”, otherwise it is a two-step processing method.

Table 2.1 Formulations^a of PLA/TSBP and PLA/SBP composites

	Formulation	PLA	SBP	TSBP ^b	PLA-g-MA	PBAT-g-MA	PBAT
	uncompatibilized	60		40			
	PBAT-3	60		40			3
	PLA-g-MA-1	60		40	1		
Two-step	PLA-g-MA-3	60		40	3		
PLA/TSBP	PLA-g-MA-5	60		40	5		
	PBAT-g-MA-1	60		40		1	
	PBAT-g-MA-3	60		40		3	
	PBAT-g-MA-5	60		40		5	
	One-step						
One-step	PLA-g-MA-3	60	40		3		
PLA/SBP	One-step						
	PBAT-g-MA-3	60	40			3	
Neat PLA	PLA	100					

^a all the numbers represent for the wt %. ^b Dry weight.

Microscopy. Morphology of the composites was examined by field emission scanning electron microscopy (FE SEM, Quanata 200F). Several pieces of composite sheets were stacked and glued together by epoxy resin and cut with a microtome to investigate phase structure of the composites. Tensile fracture surfaces were also prepared and studied. All samples were sputter coated with a layer of gold prior testing.

Tensile test. This test is according to ASTM standard (ASTM D638, type III). The extruded sheets were cut using a dog-bone mode. Tests were performed on a screw-driven universal testing machine (Instron 4466) equipped with a 10 kN electronic load cell and mechanical grips. Crosshead speed was set as 5 mm/min and strain was measured by a 25-mm extensometer (MTS 634.12E-24). At least 7 replicates were tested for each formulation to minimize the error.

Dynamic Mechanical Analysis (DMA). A dynamic mechanical analyzer (TA Q800) was used to examine the dynamic mechanical properties of SBP/PLA composites. Samples with dimensions of approximately $25 \times 12 \times 1$ mm were prepared with a milling machine and tested by a single-cantilever fixture at a frequency of 1 Hz. Strain was fixed at 0.03% and all the tests were conducted from -50 °C to 150 °C under a heating speed of $2^{\circ}\text{C}\cdot\text{min}^{-1}$.

Differential Scanning Calorimetry (DSC). A DSC (Mettler Toledo 822e) was employed to study the crystallization behavior of PLA/SBP composite. About 6 mg samples was cut from the extruded sheet and were sealed in a $40\text{-}\mu\text{m}$ aluminum pan. Another same sealed aluminum pan without sample was used as reference. Tests were conducted from 25 °C to 180 °C at a heating/cooling rate of 10 °C $\cdot\text{min}^{-1}$. All the samples were first scanned to remove thermal history and isothermal at 180 °C for 2 min, and then cooled to 25 °C for 2 min. After that,

samples were heated again to 180 °C. Second heating curves were analyzed and studied in this work.

2.3 Results and Discussion

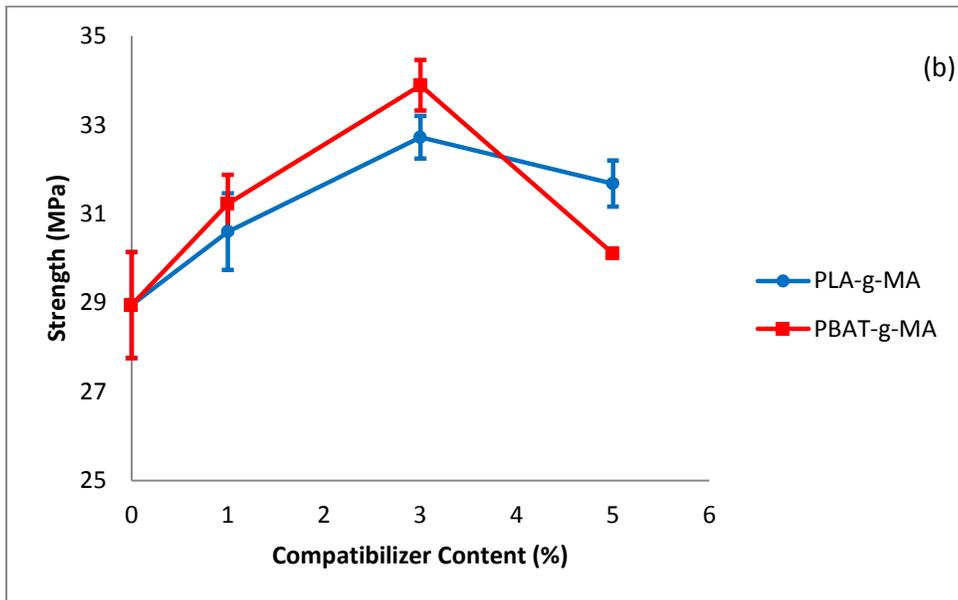
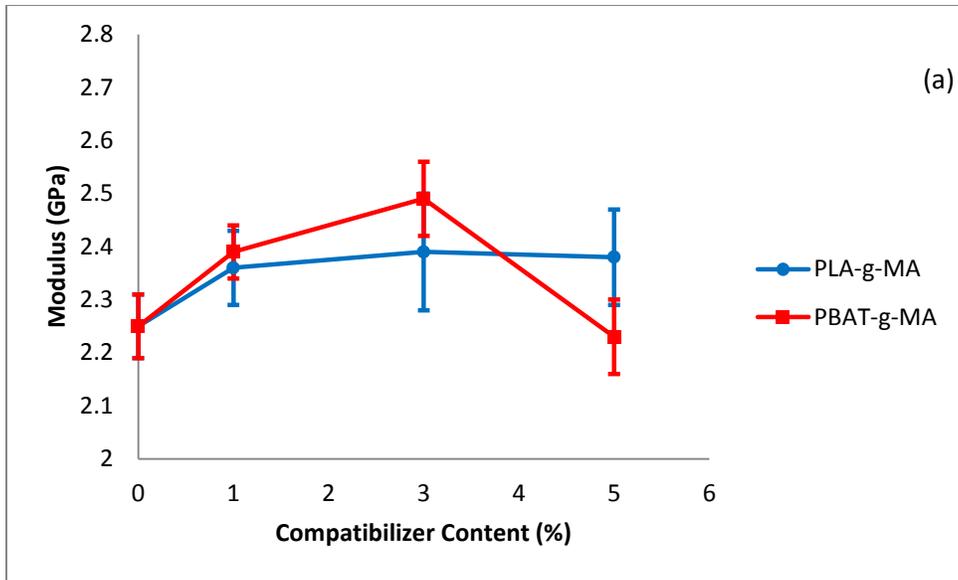
2.3.1 Tensile Properties

Table 2.2 summarizes the tensile properties of PLA composites prepared with the SBP filler and TSBP. A statistical analysis using Tukey's method was applied on these results to evaluate whether the properties are significantly different with each other. Confidence level which is an indication of the dependability of an estimate was set at 95%. The letter(s) next to each value denote whether they were statically significant different from each other Therefore, as shown in Table 2, compatibilizer type, compatibilizer concentration and processing method have significant effects on the tensile properties of PLA/SBP composites. For example, with 3 wt% compatibilizers, PBAT-g-MA-3 exhibited an elongation of 3.56 % and strength of 33.89 MPa, which were 12% and 5% higher than that of PLA-g-MA-3, 50% and 17% higher than that of the uncompatibilized one, respectively.

Table 2.2 Mechanical properties of TSBP/PLA and SBP/PLA composites

Compatibilizers		Strength MPa		Elongation %		Modulus GPa	
PLA/TSBP	uncompatibilized	29.0±0.7	F	2.4±0.9	F	2.3±0.6	BC
	PBAT-3	30.3±0.7	DE	2.5±0.2	EF	2.2±0.1	C
	PLA-g-MA-1	30.6±1.2	CDE	2.8±0.2	DE	2.4±0.1	ABC
	PLA-g-MA-3	32.7±0.9	AB	3.2±0.3	BC	2.4±0.1	AB
	PLA-g-MA-5	31.7±0.5	BC	2.7±0.2	EF	2.4±0.1	AB
	PBAT-g-MA-1	31.2±0.5	CDE	3.0±0.2	CD	2.4±0.5	AB
	PBAT-g-MA-3	33.9±0.7	A	3.6±0.2	A	2.5±0.1	A
	PBAT-g-MA-5	30.1±0.6	EF	3.5±0.3	AB	2.2±0.1	C
PLA/SBP	One-step PLA-g-MA-3	31.7±0.8	BCD	2.6±0.1	EF	2.3±0.6	BC
	One-step PBAT-g-MA-3	33.1±0.9	A	2.8±0.2	DE	2.4±0.1	A
	Neat PLA	PLA	67.7±1.2		3.5±0.1	3.4±0.1	

^aData was analyzed with general linear modal using SAS software. Tukey's method was applied to our results with confidence level of 95%. Values with different letters mean they are significantly different with each other.



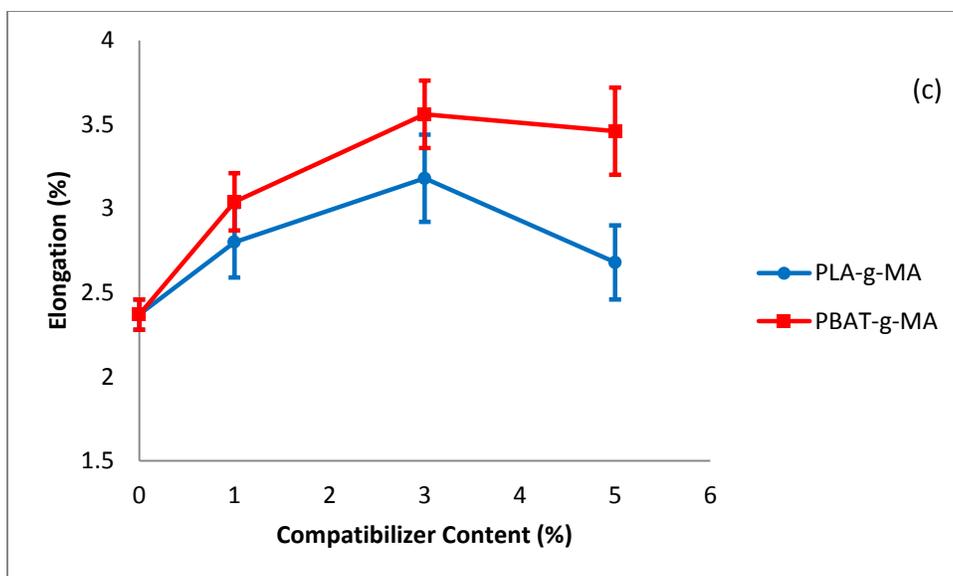


Fig. 2.1 Comparison of effect of PLA-g-MA and PBAT-g-MA on tensile properties of PLA/TSBP composite sheets: (a) Modulus, (b) Tensile strength, (c) Elongation.

Neat PLA exhibited fairly high strength and modulus. Like many other highly filled polymer materials, the strength of the PLA/SBP composites suffered a great reduction. The uncompatibilized sample exhibited a tensile strength of 28.95 MPa and a modulus of 2.25 GPa which were much lower than that of neat PLA. With the addition of only 1 wt % of PBAT-g-MA, tensile strength and Young's modulus increased to 31.23 MPa and 2.39 GPa, respectively. With 3 wt % PBAT-g-MA, tensile strength and Young's Modulus further increased to 33.89 MPa and 2.49 GPa, respectively. However, by further increasing PBAT-g-MA to 5 wt%, strength and modulus showed little changes. As shown in Fig. 2.1, changes of properties with the addition of PLA-g-MA and PBAT-g-MA show a similar pattern. SBP is hydrophilic whereas PLA is hydrophobic, compatibilizing the interface for improved adhesion is necessary. The maleic anhydride group can react with some of the functional groups in SBP so as to improve interfacial adhesion between SBP and PLA. Therefore, it is expected that tensile properties increased with

compatibilizer content. However, if excessive amounts (5 wt%) of compatibilizer was introduced, the interface was saturated and hence tensile properties were no longer improved. A emulsification curve study by Li (Li and Favis 2002) using copolymer as compatibilizer in several polymer blend systems also found that an initial increase of copolymer significantly decreased the size of the dispersed phase but after a critical value is reached, it equilibrated to a constant value.

It was evident that PBAT-g-MA was a slightly more effective compatibilizer than PLA-g-MA (Fig. 2.1). To better understand the role of PBAT in the PLA/TSBP system, a control with 3 wt% of PBAT was prepared. It is interesting to note that the addition of PBAT slightly improved tensile strength and elongation as shown in Table 2.1. PBAT can serve as a good polymer modifier to increase the ductility of PLA through the debonding induced shear yielding mechanism. (Jiang et al. 2006) Therefore, improved tensile properties were achieved.

Typical tensile behaviors of two-step PLA/TSBP and one-step PLA/SBP composites are shown in Fig. 2.2. Generally, the two-step PLA/TSBP composite exhibited better tensile properties than that of the one-step PLA/SBP composite, especially the elongation. For example, with 3 wt% of PBAT-g-MA added, one-step PLA/SBP composite exhibited an elongation of 2.79 whereas two-step PLA/TSBP composite exhibited an elongation of 3.56. In the two-step processing method, the cell wall was broken and water-soluble pectin was released under high shear stress during the first extrusion. Therefore, TSBP of two-step had better deformability than SBP of one-step and it was turned into fine thread shapes during compounding with PLA. This kind of shape provided more specific area. Also, water which can easily lead to hydrolysis of PLA has more opportunities for contact with the PLA matrix in one-step processing. Therefore, these two reasons account for the better tensile properties in the two-step PLA/TSBP composites.

It should be pointed out that though the compatibilized PLA/TSBP composites demonstrated increased tensile strength, modulus and even elongation, the improvements were still very limited and the composites were still brittle.

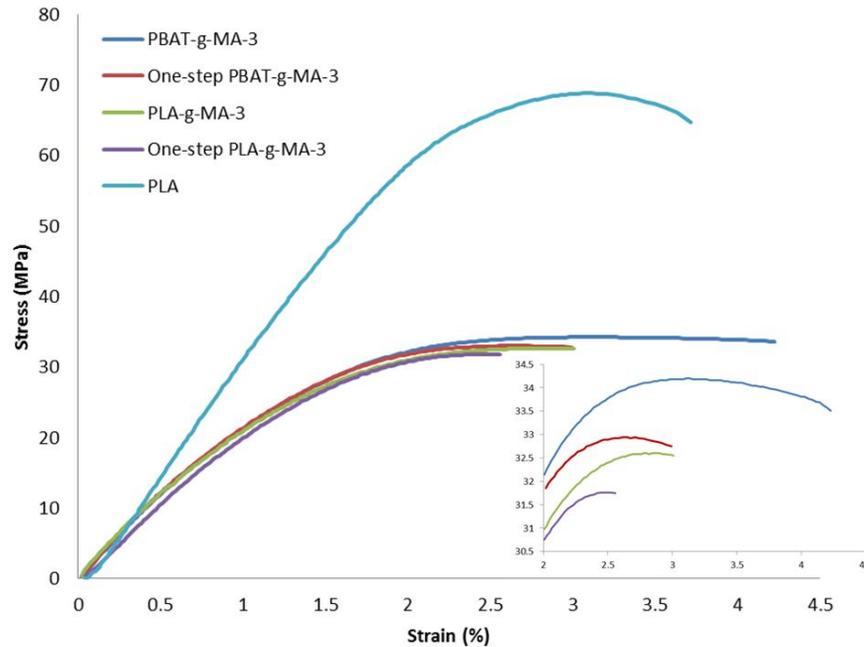


Fig. 2.2 Stress-Strain curves showing comparison of one-step PLA/SBP and two-step PLA/TSBP composite with 3 wt% compatibilizers as well as neat PLA.

2.3.2 Morphology of Tensile Fracture Surfaces

Fig.2.3 shows the tensile fracture surfaces of PLA/TSBP, PLA/SBP composites as well as neat PLA. Neat PLA exhibited a very flat surface due to a brittle failure (Fig. 2.3a). For the uncompatibilized PLA/TSBP composite (Fig. 2.3b), large SBP particles are clearly seen with little wetting noted. This evidence suggests the weak interface adhesion between PLA and SBP. Addition of 3 wt% PBAT (Fig. 2.3c) appeared to slightly increase the plastic deformation of the PLA matrix as the surface appeared rougher. With the addition of compatibilizers, particle size

Due to the plasticization effect of water and glycerol during compounding, SBP is turned into thermoplastic-like SBP (TSBP) by extrusion. TSBP can deform and flow under shear force like a thermoplastic during compounding with PLA. The hydrophilic TSBP and hydrophobic PLA are immiscible. It is well accepted that viscosity ratio, composition, interfacial adhesion, etc. will have an effect on the morphology of two immiscible polymers. Because the TSBP was a minor phase and appeared to have a higher viscosity, it was dispersed in the PLA matrix as droplets. Droplets can be stretched into threads and subsequently break up into smaller droplets when enough residence time is allowed. Conversely, small droplets can also coalesce to form a bigger one. Therefore, it is generally believed that there exists a balance between the threads breaking up and the droplets coalescing. Phase structures of the PLA/TSBP composite with different amounts of compatibilizers are shown in Fig. 2.4. TSBP phase appeared to be ellipse and were well dispersed in the PLA matrix. It is evident that particle size of SBP decreased with increasing compatibilizer concentration. At low compatibilizer concentration (1 wt%), interstices between SBP and PLA phases are clearly observed, but interstices became less at higher concentration (5 wt%). These results suggest that better wettability was achieved. Both PBAT-g-MA and PLA-g-MA could react with SBP and enhance interfacial bonding between TSBP and PLA phases. The SBP particles presented remarkably different morphological structures in PLA/TSBP and PLA/SBP (Figs. 2.4 d & d'). Compared to two-step composites, one-step PLA/SBP composites exhibited a much bigger particle size of SBP. Water and glycerol plasticized TSBP has better deformability than dry SBP. Therefore, when TSBP was compounded with PLA, it was easy to break and exhibited smaller particle size. Evidence of large interstices in the one-step PLA/SBP composite suggests that the wettability of SBP particles by PLA was poor.

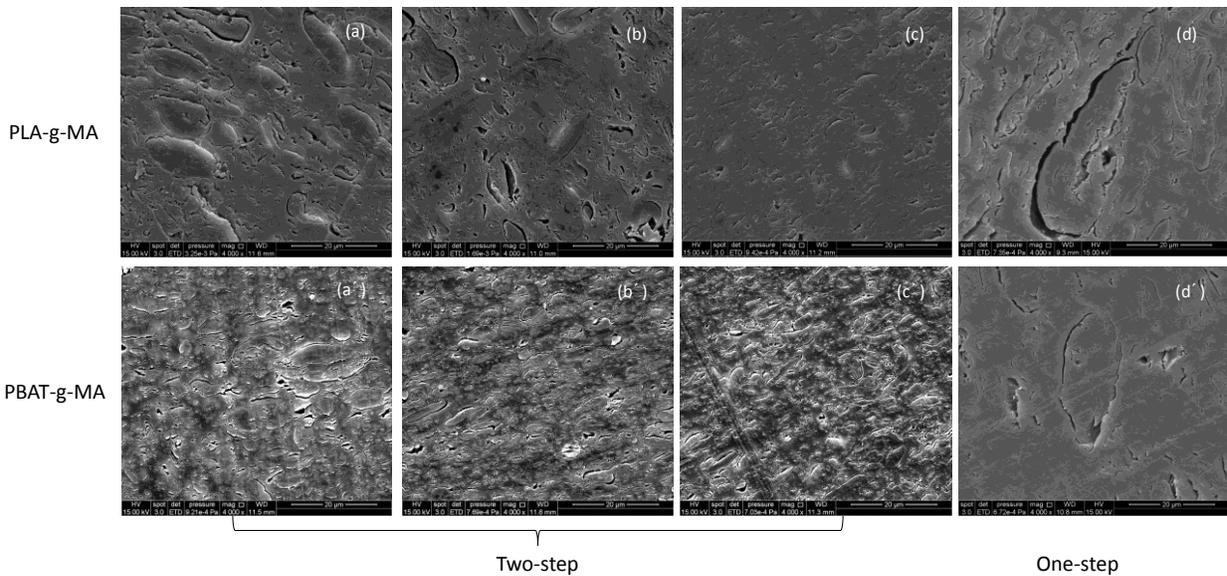


Fig. 2.4 SEM micrographs of microtomed surfaces of PLA/TSBP and PLA/SBP. (a) PLA-g-MA-1, (b) PLA-g-MA-3, (c) PLA-g-MA-5, (a') PBAT-g-MA-1, (b') PBAT-g-MA-3, (c') PBAT-g-MA-5, (d) One-step PLA-g-MA-3, (d') One-step PBAT-g-MA-3.

To better evaluate the morphology and structure of TSBP in the PLA matrix, TSBP particles were extracted in as shown in Fig. 2.5. Without compatibilizers (Fig. 2.5a), SBP particle is in approximately a round shape with large particle size. With addition of 1 wt% of PLA-g-MA (Fig. 2.5 b), particle size decreased dramatically and the round shape SBP particle was transformed into a fine thread shape. Further increase of PLA-g-MA content decreased TSBP particle size. The aspect ratio increased largely compared to the uncompatibilized one. The threaded shape of SBP particles was more effective to transfer the shear stress from the matrix than the roundabout particles and accounts for the improved mechanical properties.

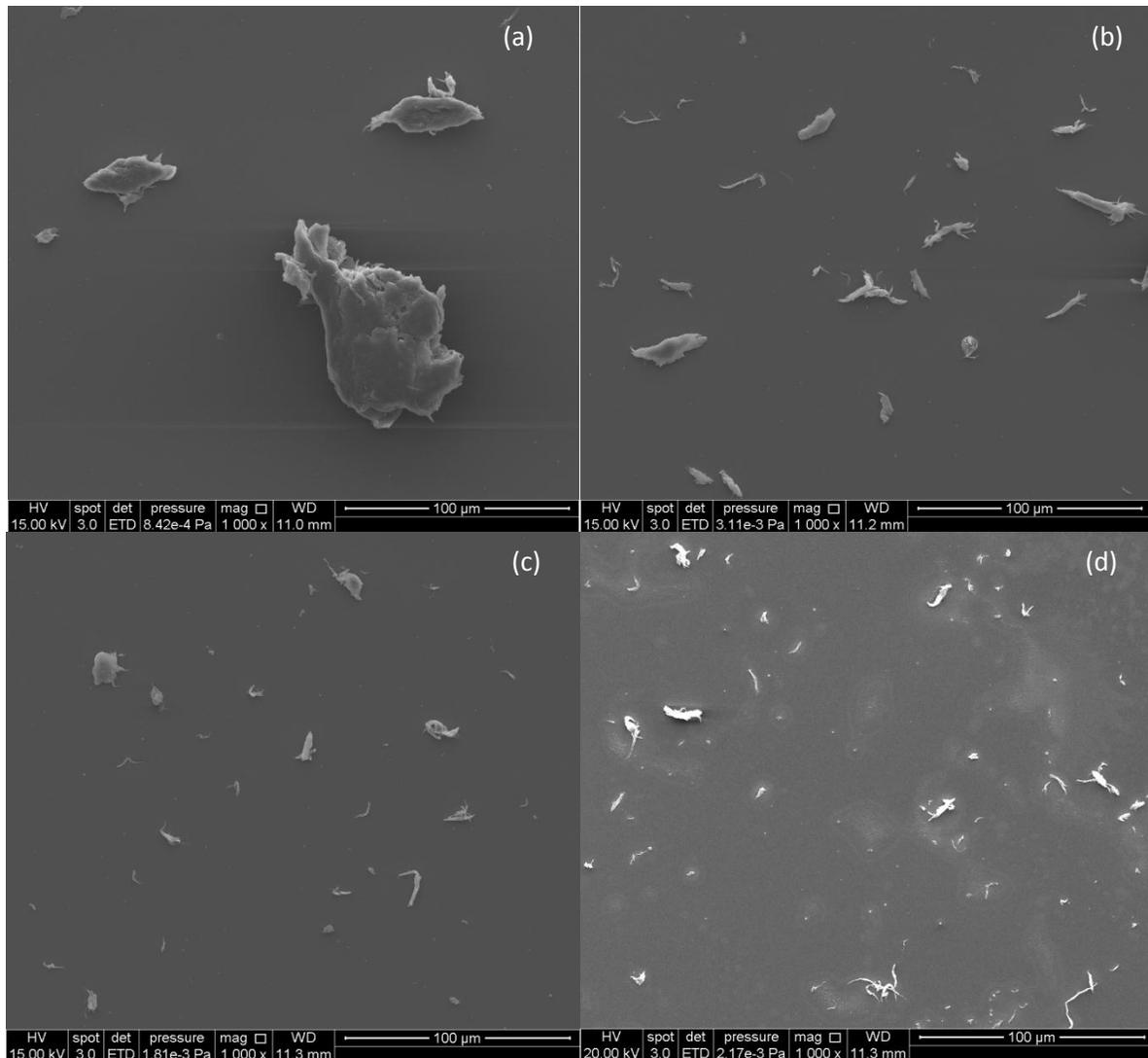


Fig. 2.5 SEM images of chloroform extraction of PLA/TSBP using PLA-g-MA as compatibilizer. (a) uncompatibilized, (b) PLA-g-MA-1, (c) PLA-g-MA-3, (d) PLA-g-MA-5.

2.3.4 Dynamic Mechanical Properties

Fig. 2.6 shows the storage moduli (E') of PLA/TSBP and PLA/SBP composite. All the composites displayed a sharp drop around 60 °C and a moderate rise around 90 °C. The former corresponded to the glass transition temperature (T_g) of PLA, whereas the latter indicated cold

crystallization of PLA (85-100 °C) had occurred. Obviously, storage moduli of PLA/SBP and PLA/TSBP composites precipitated more than that of neat PLA with temperature ranging from -20 °C to 50 °C. This was probably because water and glycerol in TSBP were frozen at low temperature and gradually thawed as temperature increased. Table 2.3 gives the comparison of storage moduli for various samples at several selected temperatures. The influence of compatibilizer on E' was similar to that on tensile properties (Table 2.2), and this was true even in high temperature (120 °C). Chemical interaction occurs when the compatibilizer was introduced onto the surface of SBP particles. Storage modulus increased with compatibilizer concentration until interface was saturated. PLA/TSBP composite with 3 wt% of both kinds of compatibilizers exhibited the highest storage modulus (Fig. 2.6 a&b). This result further demonstrated that both PLA-g-MA and PBAT-g-MA were effective compatibilizers and the two-step processing method was better than the one-step one.

Table 2.3. Storage moduli of PLA/TSBP and PLA/SBP composite at different temperatures.

Sample	E'		
	Pa		
	25°C	60°C	120°C
Unompatibilized	2.62E+09	4.42E+08	2.01E+08
PBAT-3	2.77E+09	5.17E+08	1.89E+08
PLA-g-MA-1	2.99E+09	6.34E+08	2.61E+08
PLA-g-MA-3	3.09E+09	6.67E+08	2.84E+08
PLA-g-MA-5	3.12E+09	6.12E+08	2.81E+08
PBAT-g-MA-1	3.08E+09	6.70E+08	2.97E+08
PBAT-g-MA-3	3.20E+09	6.04E+08	3.38E+08
PBAT-g-MA-5	3.03E+09	5.17E+08	2.37E+08
One-step PLA-g-MA-3	2.97E+09	5.91E+08	2.26E+08
One-step PBAT-g-MA-3	3.12E+09	5.15E+08	2.10E+08
PLA	3.28E+09	7.19E+08	1.68E+08

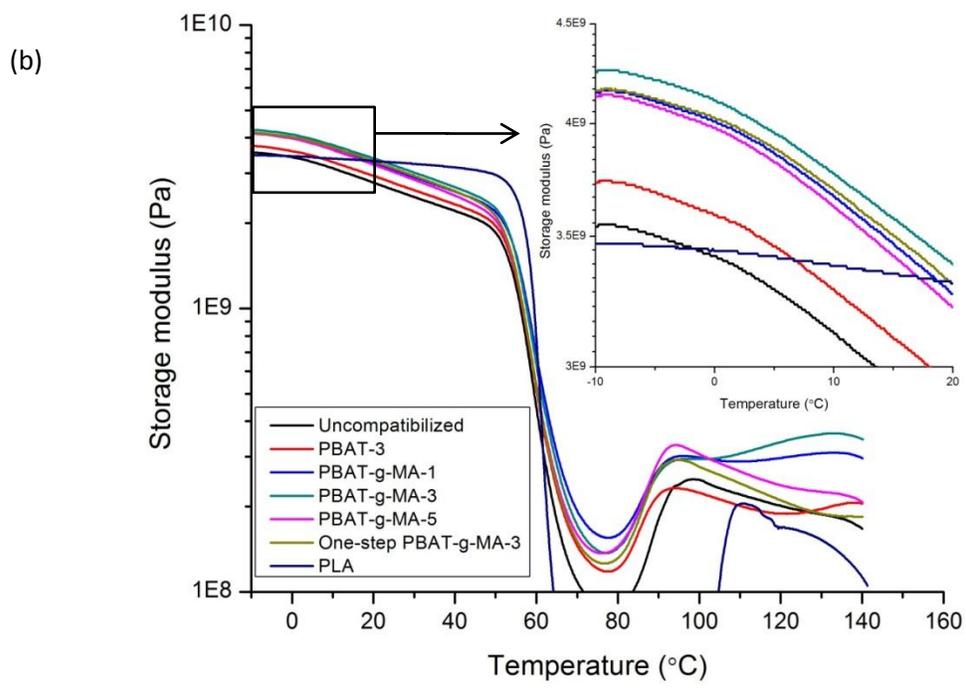
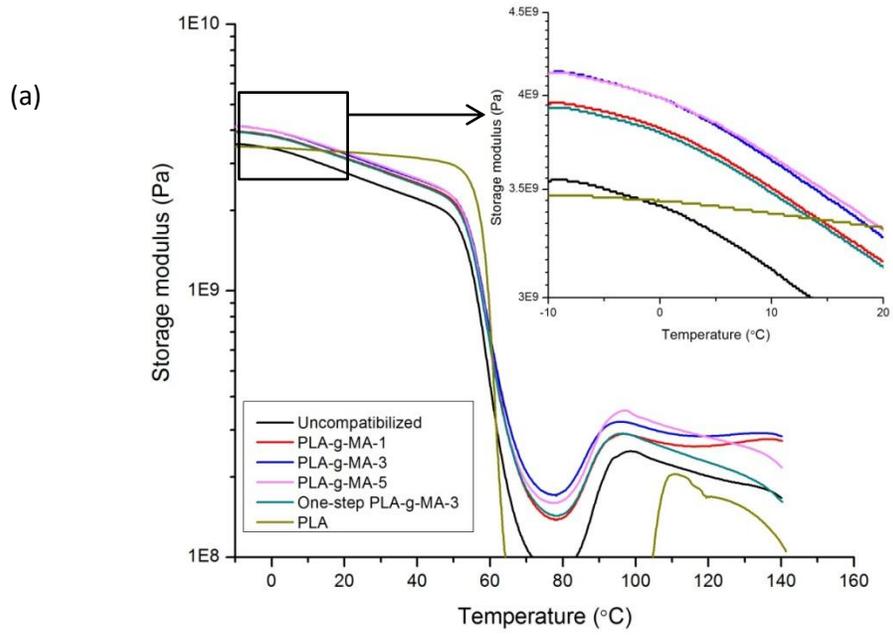


Fig. 2.6. Effect of compatibilizer on storage modulus of PLA/SBP composites. (a) PLA-g-MA, (b) PBAT-g-MA.

Fig 2.7 gives the comparison of damping ($\tan \delta$) curves of selective PLA/TSBP and PLA/SBP composites. The damping peak of neat PLA was very sharp and narrow. Addition of 40 wt% of TSBP lowered and broadened the peak significantly. Above the T_g (around 65 °C), PLA was in a rubbery state and very soft. Because the incorporated SBP was still in its glassy state in the glass transition range of PLA, the height of the damping peak of PLA in the composites was lowered greatly. The broadening of the peak indicated the existence of certain interactions between the molecules of these two components. Addition of compatibilizer resulted in further reduction in height and broadening of the PLA damping peak. This result is expected because the compatibilizer further improved interfacial bonding. TSBP particles became a fine thread shape after compatibilizers were introduced (Fig. 2.5) which might also exert restriction on PLA molecular movement. With 3 wt% of PLA-g-MA, the damping peak of the two-step PLA/TSBP composite was slightly lower than that of the one-step PLA/SBP composite. In the two-step process, SBP particles deformed better than that in the one-step process, so smaller particles were resulted as shown in Fig. 2.4. Percolated structure of SBP with smaller particle size had more effective restriction on molecular movement of PLA. When PBAT-g-MA was used as the compatibilizer, damping peak increased as more compatibilizer was added. This is expected because PBAT is a flexible polymer and is rubbery in the glass transition range of PLA .

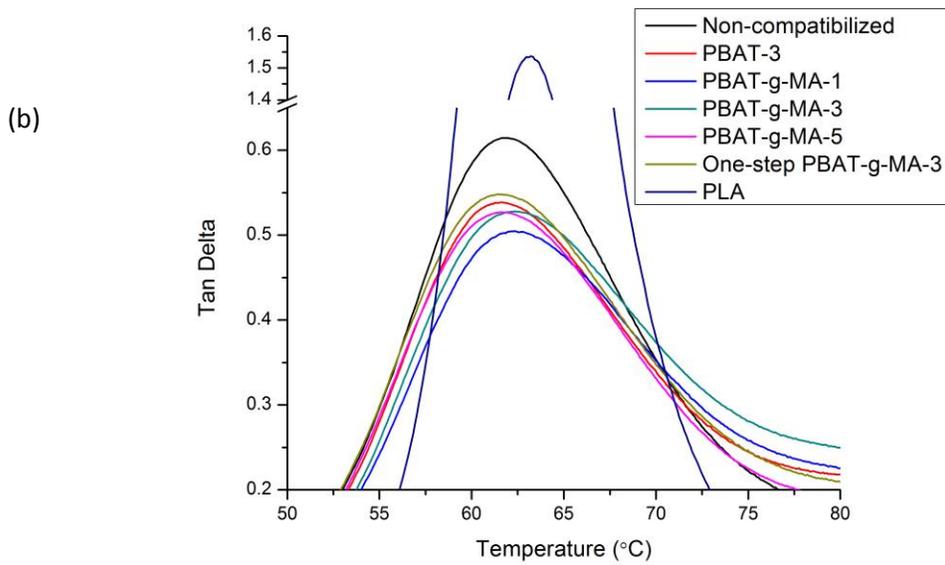
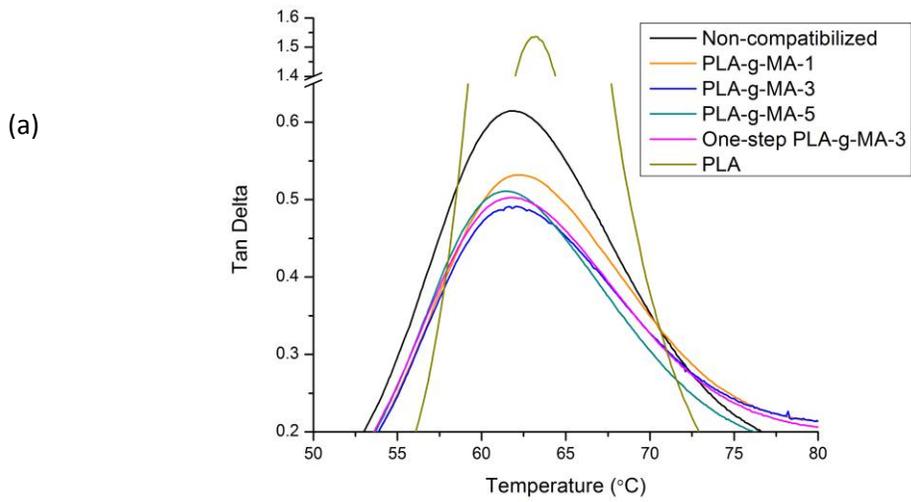


Fig. 2.7. Effect of compatibilizer on damping of PLA/SBP composites. (a) PLA-g-MA, (b) PBAT-g-MA.

2.3.5 Crystallization

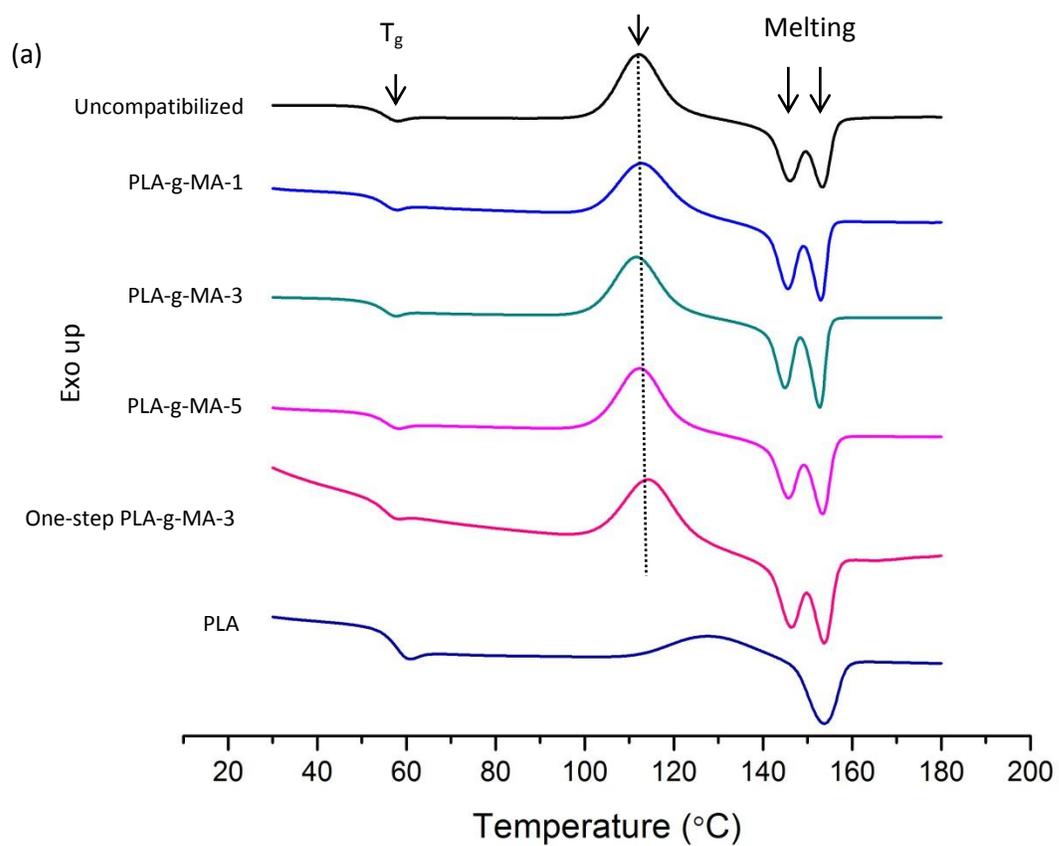
Fig. 2.9 shows the DSC thermograms of PLA/SBP composites during the second heating scan. The first thermal transition corresponded to the glass transition (T_g) of PLA. Exothermic peak and endothermic peak represented cold crystallization and melting, respectively. Incorporation of SBP or TSBP decreased with cold crystallization temperature and narrowed the cold crystallization peak considerably (Figs. 2.8 a&b), because SBP, as a foreign matter, acted as a heterogeneous nucleating agent and hence increased crystallization. Incorporation of PBAT or PBAT-g-MA further narrowed the cold crystallization peak and lowered the cold crystallization temperature about 8 °C (Fig 2.8 b), suggesting an enhanced crystallization ability and rate. This result is consistent with a study of PLA/PBAT blends by Jiang et al. (Jiang et al. 2006) It is interesting to note that PLA/SBP and PLA/TSBP composites exhibited a bimodal peak compared to neat PLA. The melting peak with lower melting temperature (T_{m1}) is probably caused by less than perfect crystal lamellars induced by heterogeneous nucleation (Jiang et al. 2006). These crystals experienced melting, recrystallization, and then melted again at higher melting temperature (T_{m2}).

Table 2.4 DSC results of PLA/TSBP and PLA/SBP composites.

Sample	cold crystallization			melting		
	T _g (°C)	T _{cc} (°C)	ΔH _{cc} ^a (J/g)	T _{m1} (°C)	T _{m2} (°C)	ΔH _m ^a (J/g)
Uncompatibilized	56.13	112.17	24.7	145.83	153.50	26.0
PBAT-3	57.37	105.67	25.0	144.67	154.17	25.6
PLA-g-MA-1	55.68	112.83	24.0	145.50	153.17	26.3
PLA-g-MA-3	56.52	111.50	26.3	146.17	153.67	26.9
PLA-g-MA-5	55.94	111.00	28.7	145.67	153.50	29.3
PBAT-g-MA-1	56.04	103.86	25.9	143.07	152.51	26.8
PBAT-g-MA-3	55.57	102.33	24.1	142.67	152.50	25.2
PBAT-g-MA-5	55.95	105.35	25.0	143.55	153.09	25.7
One-step PLA-g-MA-3	56.06	114.33	26.6	147.17	153.83	29.3
One-step PBAT-g-MA-3	56.75	105.00	27.7	144.33	154.00	29.2
PLA	57.58	126.33	6.8		153.83	16.1

^a Data corrected for the percentage of PLA in the composite

Cold crystallization



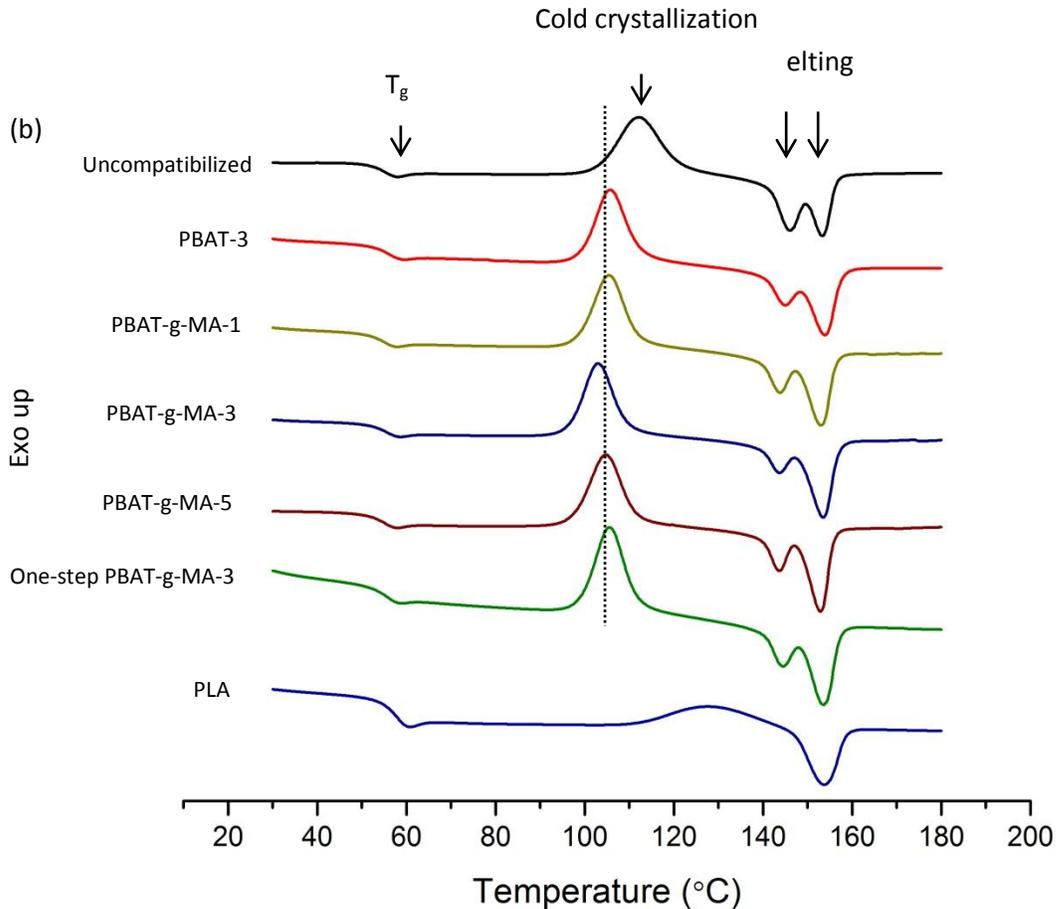


Fig. 2.8 DSC thermograms of PLA/SBP composites during the second heating scan comprising a) PLA-g-MA, b) PBAT-g-MA.

2.4 Conclusions

Dried SBP was turned into thermoplastic-like SBP with the presence of water and then was compounded with PLA glycerol in this study. Properties of the resulting composites were largely affected by compatibilizer type, concentration and processing method. Both PLA-g-MA and PBAT-g-MA proved to be effective compatibilizers. Both improved mechanical properties significantly, but PBAT-g-MA proved to be a little better due to the toughening effect on the

PLA matrix. Mechanical properties also increased with compatibilizer concentration until the interface was saturated (at ~3 wt%). Compatibilized composites exhibit fine and thread shape of SBP particles. Composites made by the two-step processing method exhibited better performance and smaller particle size of SBP phase than that of the one-step processing method because most of plasticizers are believed to reside in SBP phase. Dynamic mechanical properties are affected by dispersion and phase structure of SBP particles. The change of storage modulus was in accordance with the change of tensile modulus. The damping peak of PLA was lowered by the addition of compatibilizer due to formation of fine SBP particles which had a higher restriction effect on PLA molecular chain movement. DSC study demonstrated SBP particles induced heterogeneous nucleation. Addition of PBAT improved flexibility of PLA matrix.

Reference

- Chen, F. (2010). Investigation of soy protein blends prepared by simultaneous plasticization and mixing.
- Chen, F., L. Liu, et al. (2008). "Performance Enhancement of Poly(lactic acid) and Sugar Beet Pulp Composites by Improving Interfacial Adhesion and Penetration." Industrial & Engineering Chemistry Research **47**(22): 8667-8675.
- Dufresne, A., J. Y. Cavaille, et al. (1997). "Mechanical behavior of sheets prepared from sugar beet cellulose microfibrils." Journal of applied polymer science **64**(6): 1185-1194.
- Finkenstadt, V., C. K. Liu, et al. (2008). "Mechanical property characterization of plasticized sugar beet pulp and poly (lactic acid) green composites using acoustic emission and confocal microscopy." Journal of Polymers and the Environment **16**(1): 19-26.
- Finkenstadt, V. L., L. S. Liu, et al. (2007). "Evaluation of poly (lactic acid) and sugar beet pulp green composites." Journal of Polymers and the Environment **15**(1): 1-6.
- Garlotta, D. (2001). "A literature review of poly (lactic acid)." Journal of Polymers and the Environment **9**(2): 63-84.
- Huda, M., L. Drzal, et al. (2006). "Wood-fiber-reinforced poly (lactic acid) composites: Evaluation of the physicomechanical and morphological properties." Journal of applied polymer science **102**(5): 4856-4869.
- Huneault, M. A. and H. Li (2007). "Morphology and properties of compatibilized polylactide/thermoplastic starch blends." Polymer **48**(1): 270-280.
- Jiang, L., M. P. Wolcott, et al. (2006). "Study of Biodegradable Polylactide/Poly(butylene adipate-co-terephthalate) Blends." Biomacromolecules **7**(1): 199-207.
- Jiang, L., J. Zhang, et al. (2007). "Comparison of polylactide/nano-sized calcium carbonate and polylactide/montmorillonite composites: Reinforcing effects and toughening mechanisms." Polymer **48**(26): 7632-7644.

- Kuuva, T., R. Lantto, et al. (2003). "Rheological properties of laccase-induced sugar beet pectin gels." Food Hydrocolloids **17**(5): 679-684.
- Leitner, J., B. Hinterstoisser, et al. (2007). "Sugar beet cellulose nanofibril-reinforced composites." Cellulose **14**(5): 419-425.
- Li, J. and B. D. Favis (2002). "Strategies to measure and optimize the migration of the interfacial modifier to the interface in immiscible polymer blends." Polymer **43**(18): 4935-4945.
- Liu, B., S. Bhaladhare, et al. (2011). "Morphology and Properties of Thermoplastic Sugar Beet Pulp and Poly(butylene adipate-co-terephthalate) Blends." Industrial & Engineering Chemistry Research.
- Liu, B., L. Jiang, et al. (2010). "Synergetic Effect of Dual Compatibilizers on in Situ Formed Poly(Lactic Acid)/Soy Protein Composites." Industrial & Engineering Chemistry Research **49**(14): 6399-6406.
- Liu, B., L. Jiang, et al. (2010). "Study of Effects of Processing Aids on Properties of Poly(lactic acid)/Soy Protein Blends." Journal of Polymers and the Environment **19**(1): 239-247.
- Liu, B., J. Zhang, et al. (2011). "Preparation and Properties of Water and Glycerol-plasticized Sugar Beet Pulp Plastics." Journal of Polymers and the Environment **19**(3): 559-567.
- Liu, H., F. Chen, et al. (2010). "Super Toughened Poly(lactic acid) Ternary Blends by Simultaneous Dynamic Vulcanization and Interfacial Compatibilization." Macromolecules **43**(14): 6058-6066.
- Liu, L. S., M. L. Fishman, et al. (2005). "Biodegradable composites from sugar beet pulp and poly (lactic acid)." Journal of agricultural and food chemistry **53**(23): 9017-9022.
- Manjula Dilkushi Silva, K., K. Tarverdi, et al. (2011). "Incorporation of wheat starch and coupling agents into poly (lactic acid) to develop biodegradable composite." Plastics, Rubber and Composites **40**(1): 17-24.

- Oosterveld, A., I. Pol, et al. (2001). "Isolation of feruloylated arabinans and rhamnogalacturonans from sugar beet pulp and their gel forming ability by oxidative cross-linking." Carbohydrate polymers **44**(1): 9-17.
- Rouilly, A., C. Geneau-Sbartā, et al. (2009). "Thermo-mechanical processing of sugar beet pulp. III. Study of extruded films improvement with various plasticizers and cross-linkers." Bioresource technology **100**(12): 3076-3081.
- Rouilly, A., J. Jorda, et al. (2006). "Thermo-mechanical processing of sugar beet pulp. I. Twin-screw extrusion process." Carbohydrate polymers **66**(1): 81-87.
- Rouilly, A., J. Jorda, et al. (2006). "Thermo-mechanical processing of sugar beet pulp. II. Thermal and rheological properties of thermoplastic SBP." Carbohydrate polymers **66**(1): 117-125.
- Turquois, T., M. Rinaudo, et al. (1999). "Extraction of highly gelling pectic substances from sugar beet pulp and potato pulp: influence of extrinsic parameters on their gelling properties." Food Hydrocolloids **13**(3): 255-262.
- Zhang, C., K. Li, et al. (2004). "Improvement of interfacial adhesion between wood and polypropylene in woodpolypropylene composites." Journal of adhesion science and technology **18**(14): 1603-1612.
- Zhang, J., L. Jiang, et al. (2006). "Morphology and properties of soy protein and polylactide blends." Biomacromolecules **7**(5): 1551-1561.
- Zhang, J. F. and X. Sun (2004). "Mechanical properties of poly (lactic acid)/starch composites compatibilized by maleic anhydride." Biomacromolecules **5**(4): 1446-1451.
- Zhu, R., H. Liu, et al. (2012). "Compatibilizing Effects of Maleated Poly (lactic acid)(PLA) on Properties of PLA/Soy Protein Composites." Industrial & Engineering Chemistry Research.

Chapter 3 Extrusion Foaming of Poly(lactic acid) and Sugar Beet Pulp Composite

ABSTRACT

In this work, thermoplastic-like sugar beet pulp (TSBP) was prepared and then was compounded with poly (lactic acid) (PLA) using PBAT-g-MA as compatibilizer. This resulting composite was foamed with a chemical blowing agent (CBA) using a continuous extrusion method. Effects of CBA content, foaming temperature and rotational screw speed on cell density, void fraction (or density reduction) and cellular morphology was tested by SEM. Foam sample with very fine cell size and high cell density were expected at low CBA content, low foaming temperature and moderate rotational screw speed, otherwise cell coalescence easily took place. Large unfoamed area was observed if CBA content was too high. Void fraction increased both CBA content and rotational speed initially, reaching a maximum level, and then decreased. In contrast, void fraction increased monotonously with foaming temperature.

Keywords: PLA, sugar beet pulp, extrusion foaming

3.1 Introduction

In recent years, poly (lactic acid) (PLA) has received more and more attention as an alternative to petroleum-based polymers. Currently, PLA is synthesized by polycondensation of lactic acids or ring opening polymerization of lactide which is the cyclic dimer of lactic acid. Lactic acid is produced from the cornstarch feed stock by fermentation. PLA is a biodegradable and compostable polyester. The modulus (3GPa) and strength (60-70 MPa) (Jiang et al. 2006) of PLA are comparable to that of traditional petroleum-based polymers such as polystyrene. However, broad application of PLA is impeded by its relatively high cost, low impact strength, low HDT and gas barrier properties. In recent years, natural fibers or natural polymers such as cellulose fibers (Huda et al. 2005), soy protein (Zhang et al. 2006) (Liu et al. 2010), sugar beet (Chen et al. 2008), starch (Manjula Dilkushi Silva et al. 2011) and wood flour (Gregorova et al. 2011) have been blended with PLA to reduce the cost and remain biodegradable at the same time. However, the already low ductility and impact strength are further highly compromised. For example, when 30 wt% of soy protein was added into PLA, elongation decreased from 2.90 to 1.26% and impact strength decreased from 2.39 to 1.19 KJ · m⁻² (Liu et al. 2010).

Foam technology, such as extrusion foaming, is believed to reduce material use and material weight while increase impact strength without sacrificing specific tensile modulus and strength. A typical foam extrusion includes the following steps: a) melting of the solid polymer; b) dissolution of blowing agent into the polymer melt; c) cooling of the blowing agent laden melt; d) expansion through the nucleation and bubble growth; e) stabilization of cellular structure. (Lee and Ramesh 2004) As is known to all, cellular morphology, cell density, cell size distribution, open-cell content are highly related to the properties of the foam products. In recent years, extrusion foaming of thermoplastics reinforced with various natural polymers (as filler),

such as cellulose fiber (Kuboki et al. 2009), wood flour (Matuana and Mengeloglu 2002) (Li and Matuana 2003), starch (Mihai et al. 2007) (Stagner and Narayan 2011), soy protein (Liu et al. 2011) has been investigated. Kuboki et al. (Kuboki et al. 2009) studied the foaming behavior of HDPE reinforced with cellulose fiber and observed that fiber length is unrelated to cellular morphology. Matuana and Mengeloglu (Matuana and Mengeloglu 2002) found that bound water from the cell wall can be effectively utilized as a blowing agent. Water as a blowing agent was also reported by Zhang and Sun (Zhang and Sun 2007) who studied foaming behavior of PLA/starch system and discovered that talc was an effective nucleating agent. Cell size distribution decreased significantly when 2% of talc was added. A study from our group (Liu et al. 2011) showed that foaming temperature, CBA content as well as interfacial modifier significantly affected bulk density and cell density.

Sugar beet pulp (SBP), a low value residue after sugar extraction, has attracted intensive research interest. SBP can be used alone (Liu et al. 2011) for plastics or blended with other polymers (Chen et al. 2008) (Liu et al. 2011). Also, utilization of ingredients of SBP, such as cellulose fibrils (Leitner et al. 2007), pectin (Turquois et al. 1999) and alkaline soluble polysaccharides (Turquois et al. 1999) have been reported. In this work, SBP is introduced into PLA material because SBP and PLA are complementary to each other in a few aspects: incorporation of SBP into PLA can reduce the total cost; PLA overcomes the drawbacks of low processing ability and high water sensitivity. Because SBP contains a large amount of water-soluble pectin, it can be turned into thermoplastic-like SBP (TSBP) using a method similar to extrusion cooking. It is noted that SBP basically remains its original shape when it is used as filler in polymer blends, whereas TSBP turns into the form of fine threads. (Liu et al. 2011)

Incorporation of SBP into PLA results in high viscosity, so plasticizer and lubricant were added to improve processibility and reduce melt flow activation energy.

Foaming application of PLA/TSBP composites was first investigated in this work. Effects of foaming temperature, rotational screw speed and CBA content on PLA/TSBP composite foam was studied. A two-step method which was found to provide better properties was employed in this work. First, TSBP was made through extrusion with water as the plasticizer and then was compounded with PLA. Second, TSBP was compounded with PLA. The compounds in pellets were finally extrusion foamed with CBA. This study aims to investigate the cellular morphology, cell density and void fraction.

3.2 Experimental

Materials. PLA that was employed in this study was NaturalWorks PLA 4042D. SBP (Fibrex 575) was obtained from Nordic Sugar Company, had a particle size of less than 0.032 mm. Every 100 g of such SBP is composed of approximately 67 g Fibre (42% Hemicellulose, 28% Cellulose, 27% Pectin and 3% Lignin), 8 g Protein, 5.5 g Carbohydrate, 5.5 g Sugar, 1 g fat, 4 g Minerals and roughly 6g moisture. MA grafted PBAT was prepared by ourselves, using the reactive extrusion method. Acetyltri-*n*-butyl citrate (citroflex A-4) was obtained from Morflex Inc. Alkene bis fatty amide (Glycolube WP2200) was received from Lonza Inc. Chemical Blowing Agent (CBA) used in this study is 4-methylbenzene-1-(Afrifah and Matuana 2010)sulfono-hydrazide containing 5% CaCO₃ (Celogen TSH-C) and was obtained from Chemtura (Middlebury, CT). All the materials above are used as received without any further purification.

Preparation of TSBP and blending of PLA with TSBP. The methods for TSBP preparation and blending were essentially the same as those in Chapter 2 with a few modifications. First, only water (35 wt%) was used as a plasticizer in preparation of TSBP. Second, to improve processibility of the composite, only 20 wt% of TSBP was compounded with PLA. Finally, a lower zone temperature profile of 90, 120, 140, 150, 160, 160, 155, 150 °C from the first heating zone to die adaptor, was adopted.

Extrusion foaming of TSBP/PLA composite. Pelletized composites were dried at 70 °C for 24 h to remove the residual water before foam processing. The same twin-screw extruder was employed for foaming. A static mixer (FMX8481S, length: 5.7 in., diameter: 0.64 in., omega) and a taper filament die (1 mm in diameter) was connected to the end of extruder. The same temperature profile as that in the compounding process was adopted. The temperature of static mixer was set as 150 °C. Die temperature which is also referred to as foaming temperature varied from 130 to 160 °C. Extrusion speed varied from 40 to 100 rpm and the flow rate was 470 g·h⁻¹. CBA (0.2, 0.5, 1, 2 phr) was mixed with composite pellets before foaming extrusion.

Microscopy. The morphology of foam was examined by field emission scanning electron microscopy (FE SEM, Quanta 200F). Foam samples were immersed in liquid nitrogen for at least 20 min and then fractured to eliminate plastic deformation. All samples were sputter coated with a layer of gold to enhance conductivity prior to testing.

Density. Density of foam samples was calculated according to ASTM test method D792, using a water replacement method. Weights of sample both in air (W_a) and immersed in distilled water (W_w) were measured, respectively. The latter divided by density of water is the volume of sample. Therefore:

$$\text{Density} = 0.9975 \frac{W_a}{W_w} \quad (1).$$

5 replicates were measured for each sample to get an average.

Cell density & Void fraction. Cell density measurement was performed based on the SEM images using an image analysis software (Image J). Cell density was determined from the following equation (Matuana et al. 1998):

$$\text{Cell Density} = \left(\frac{nM^2}{A} \right)^{3/2} \frac{1}{(1-V_f)} \quad (2).$$

$$\text{Void Fraction} = 1 - \frac{\rho_f}{\rho} \quad (3).$$

where n is number of cells, A and M are the area and magnification factor of the micrograph, V_f is the void fraction, ρ_f and ρ are the densities of foamed and unfoamed samples.

3.3 Results and Discussion

3.3.1 Effect of chemical blowing agent content

SEM images in Fig 3.1 illustrate the effect of CBA content on cellular morphology of PLA/TSBP composite foam. When only 0.2 phr CBA was used, the resulting foam shows very small cell size. Cell size increased with CBA content. At high concentration of CBA content, large cells were noted to center at the inner part of the sample, which probably resulted from the coalescence of cells which occurred before the gas could escape. Large unfoamed areas were noted at 2 phr.

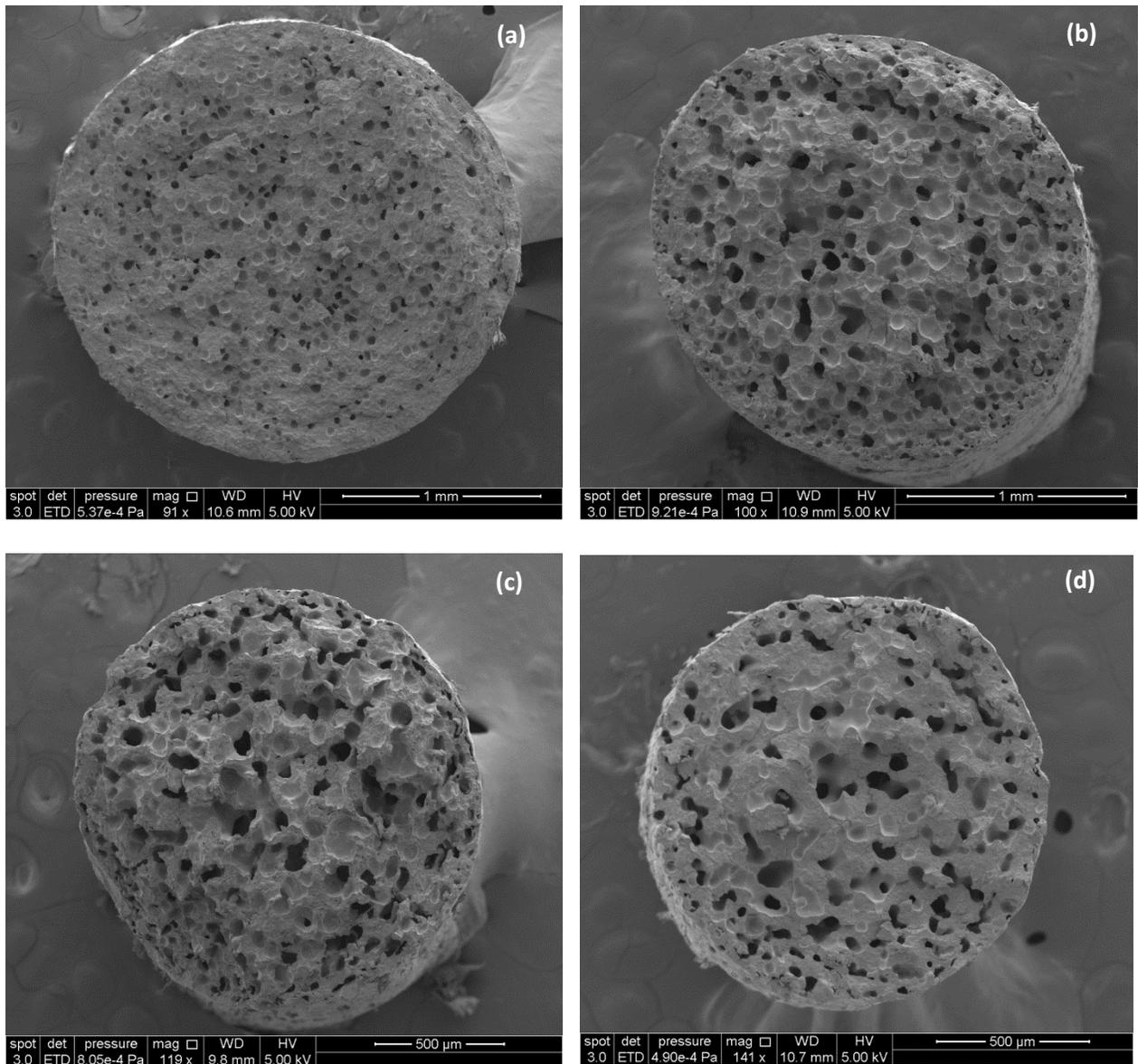


Fig. 3.1 Cell morphology of PLA/TSBP composite foamed at 150 °C with rotational speed of 60 rpm using various CBA content: (a) 0.2 phr, (b) 0.5 phr, (c) 1 phr, (d) 2 phr.

Fig. 3.2 shows the effects of CBA content on average cell density and void fraction of PLA/TSBP composite foam. Strong dependence of average cell density on CBA content was observed. With CBA content increasing from 0.2 to 2 phr, the average cell-population density

decreased uneventfully from 2.44×10^6 to 4.84×10^5 cells/cm³. The trend of cell density change was different from that of void fraction. An initial increase of void fraction was observed with CBA content increasing from 0.2 to 1 phr. Void fraction decreased as the CBA content further increased to 2 phr.

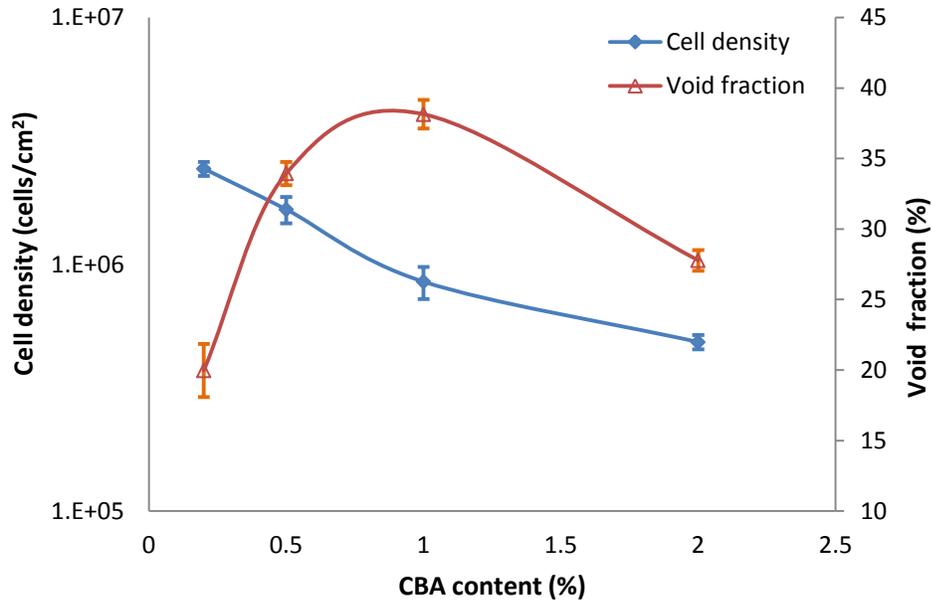


Fig. 3.2 Effect of CBA content on cell density and void fraction of PLA/TSBP composite foamed at 150 °C with a rotational speed of 60 rpm.

A typical foaming process basically includes nucleation, bubble growth, cell coalescence and solidification. In continuous extrusion foaming, polymer melt encountered a sudden pressure drop as it flowed out of the die. At this time, super-saturation was generated and it serves as main driving force for bubble nucleation and bubble growth (Lee et al. 2007). More blowing agent dissolved in polymer melt generated higher super-saturation which was favorable for cell growth. This resulted in increased cell size and high void fraction (Fig. 3.2). However, as CBA content continuing increased, an excess in the blowing agent inevitably made the cell wall thinner,

rupture and coalesce. (Fig. 3.3. c & d) It is worth mentioning that each polymer has its gas containment limit. (Li and Matuana 2003) When excessive amount of CBA (e.g. 2 phr) was introduced into the foaming process, the gas produced exceeded the gas containment limit of the polymer melt. In other words, both gas phase and gas saturated polymer melt phase coexisted. In this case, blowing gas in gas phase quickly escaped to the foam skin through the SBP network which functioned as a convenient channel (Liu et al. 2011). The blowing agent that was previously dissolved in the polymer melt phase also escaped to the foam skin through this channel instead of blowing the foam cells. Since most of the gas escaped, void fraction decreased significantly (Fig. 3.2) and a large unfoamed area was clearly observed in Fig. 3.1.(d). Unlike other foaming studies in the literature (Matuana 2008) (Liu et al. 2011), in this work the cell density initially increased and then decreased. Theoretically, cell-population density increased with CBA content because of increased nucleation rate. However, low melt strength of PLA/TSBP composite easily led to cell coalescence even at low level of CBA content (0.5 phr). Cell coalescence affected cell numbers and hence cell density. Severe cell coalescence took place and large cells were noted as CBA content increased. (Fig. 3.1)

3.3.2 Effect of foaming temperature and pressure

SEM images in Fig. 3.3 illustrate effect of foaming temperature on cellular morphology of the PLA/TSBP composite foams. Dense and small cells were acquired at the lowest temperature (130 °C). As temperature increased to 140 °C, beehive-like cellular structure was observed, indicating that the criteria optimal processing condition was satisfied. As expected, when temperature was further increased to 150 and 160 °C, as shown in Fig. 3.3 (c) and (d), cell wall rupture and cell coalescence were observed.

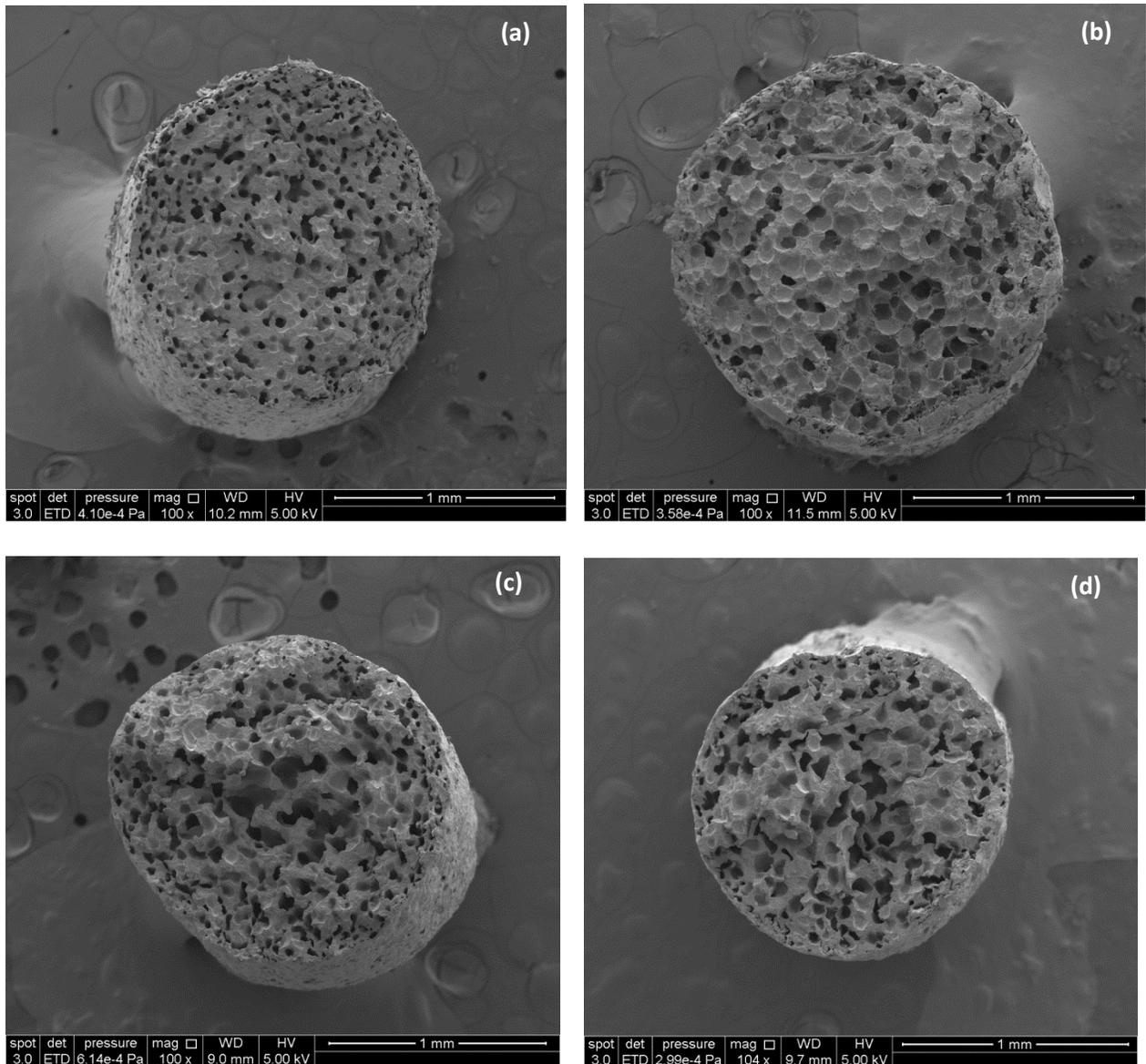


Fig. 3.3 Cell morphology of the PLA/TSBP composites foamed with 1 phr CBA and a screw speed of 60 rpm at various temperatures. (a) 130 °C, (b) 140 °C, (c) 150 °C, (d) 160 °C.

Effects of foaming temperature on average cell-population density and void fraction are presented in Fig. 3.4. When temperature increased from 130 to 160 °C, average cell density

dropped significantly from 2.21×10^6 to 7.28×10^5 cells/cm³ and void fraction increased from 30.0 to 42.3%.

Cell growth is caused by a diffusion of gas dissolved in polymer and expansion. Gas diffuses into bubbles and a pressure was generated, called bubble pressure. As long as the bubble pressure exceeds expansion pressure in viscous media, bubbles continue to grow (Lee et al. 2007) At elevated temperatures, viscosity and melt strength are highly compromised so expansion pressure is lowered. Therefore, cell growth is encouraged and high void fraction is achieved.

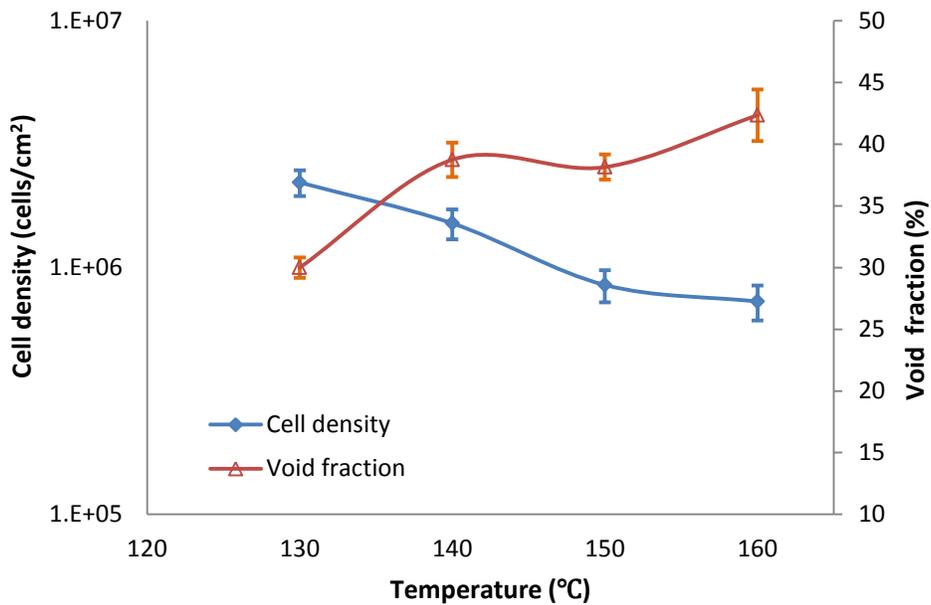


Fig. 3.4. Effect of foaming temperature on cell density and void fraction of PLA/TSBP composite foamed with 1 phr CBA and a rotational speed of 60 rpm.

Because sugar beet pulp comprised 20% of the mass in the composite, heterogeneous nucleation prevailed instead of homogeneous nucleation. Interface of PLA and SBP facilitates cell nucleation. Therefore, the classical heterogeneous nucleation rate theory can be applied to

describe this foaming system. Heterogeneous nucleation rate N_{hetero} is expressed according to following equations:

$$N_{hetero} = f_0 C_0 \exp\left(\frac{-\Delta G_{hetero}}{kT}\right) \quad (4).$$

$$\Delta G_{hetero} = \frac{16\pi\sigma^3}{3\Delta P^2} f(\theta) \quad (5).$$

$$f(\theta) = \frac{(2+\cos\theta)(1-\cos\theta)^2}{4} \quad (6).$$

where ΔG_{hetero} is the activation energy of heterogeneous nucleation, f_0 is the gas related factor, C_0 is gas concentration, σ and θ are the surface tension of polymer and gas wetting angle between polymer and nucleation particle, ΔP and T are pressure drop and temperature, respectively. (Lee and Ramesh 2004)

Among all the variables, increases in pressure drop ΔP , temperature T and/or gas concentration C_0 lead to increase in nucleation rate N_{hetero} and probably as a result, an increase in average cell-population density. However, an increase in foaming temperature T inevitably led to a decrease in pressure drop ΔP as shown in Fig. 3.5, because viscosity of polymer melt was reduced. Therefore, foaming temperature and pressure drop are competing factors in affecting heterogeneous nucleation. It is interesting to note that heterogeneous nucleation rate N_{hetero} is proportional to $\exp\left(\frac{A}{T}\right)$ for temperature, whereas $\exp\left(\frac{A}{\Delta P^2}\right)$ for pressure drop from the equation (4)-(6) (A is a function of σ and θ). Linear relationship was also found in Fig. 3.5. Up to this point, it has been concluded that nucleation rate is more sensitive with pressure drop ΔP instead of foaming temperature T . Lowering the temperature is also an effective way to improve

polymer melt strength and prevent cell coalescence. Therefore, high average cell-population density is expected at low foaming temperature.

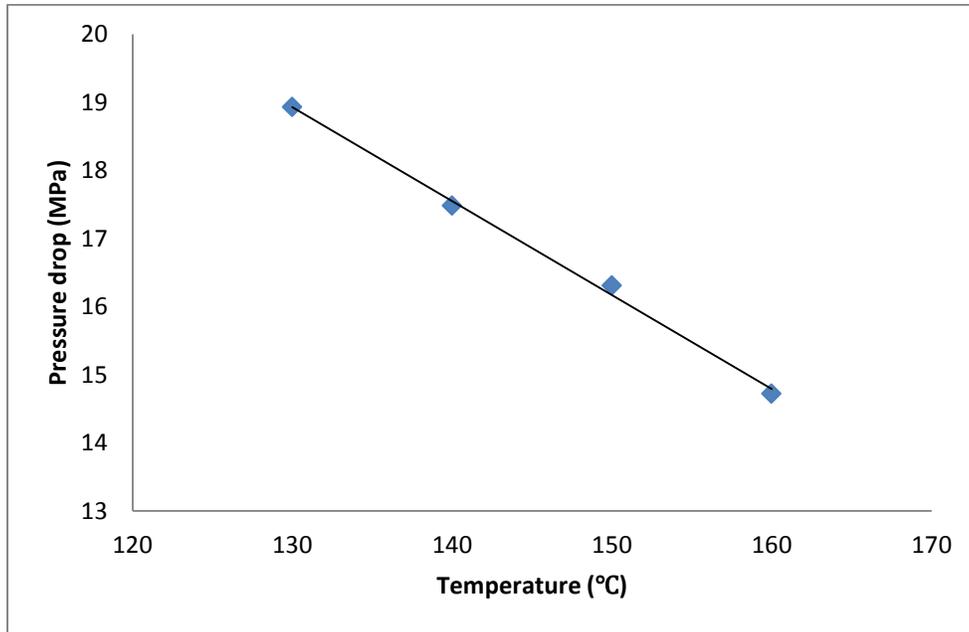


Fig. 3.5 Effect of foaming temperature on pressure drop of PLA/TSBP composite.

3.3.3 Effect of screw rotation speed

SEM images in Fig. 3.6 illustrate the effect of rotation speed on the cellular morphology of PLA/TSBP composite foam. It is evident that when screw speed increased from 40 to 60 rpm, cells become finer. Further increase of screw speed resulted in bigger cells again, and severe cell coalescence was observed at 100 rpm in Fig 3.6(d). As screw speed increases, mass flow rate increases but residence time decreases. Residence time is essentially equivalent to cell growth time, because hot extrudate was immediately dipped into water for solidification after it flows out of the die. (Han et al. 2003) Also, decomposition of the chemical blowing agent occurs at better completion with increasing residence time (Matuana et al. 1998), so large cell size is

expected because of a higher availability of blowing gas. At higher screw rotational speed (greater than 80 rpm), melt flow rate is highly increased, so shear rate in the die induced by lamellar flow is also increased. Because PLA is a pseudo-plastic material, increased shear rate from both barrel and die resulted in a shear thinning phenomenon of the composite. Faster processing speed led to lower viscosity and lower expansion pressure of melt fluid. Therefore, after the polymer melt flowed out of the die, cells grew more easily at higher screw rotation speed.

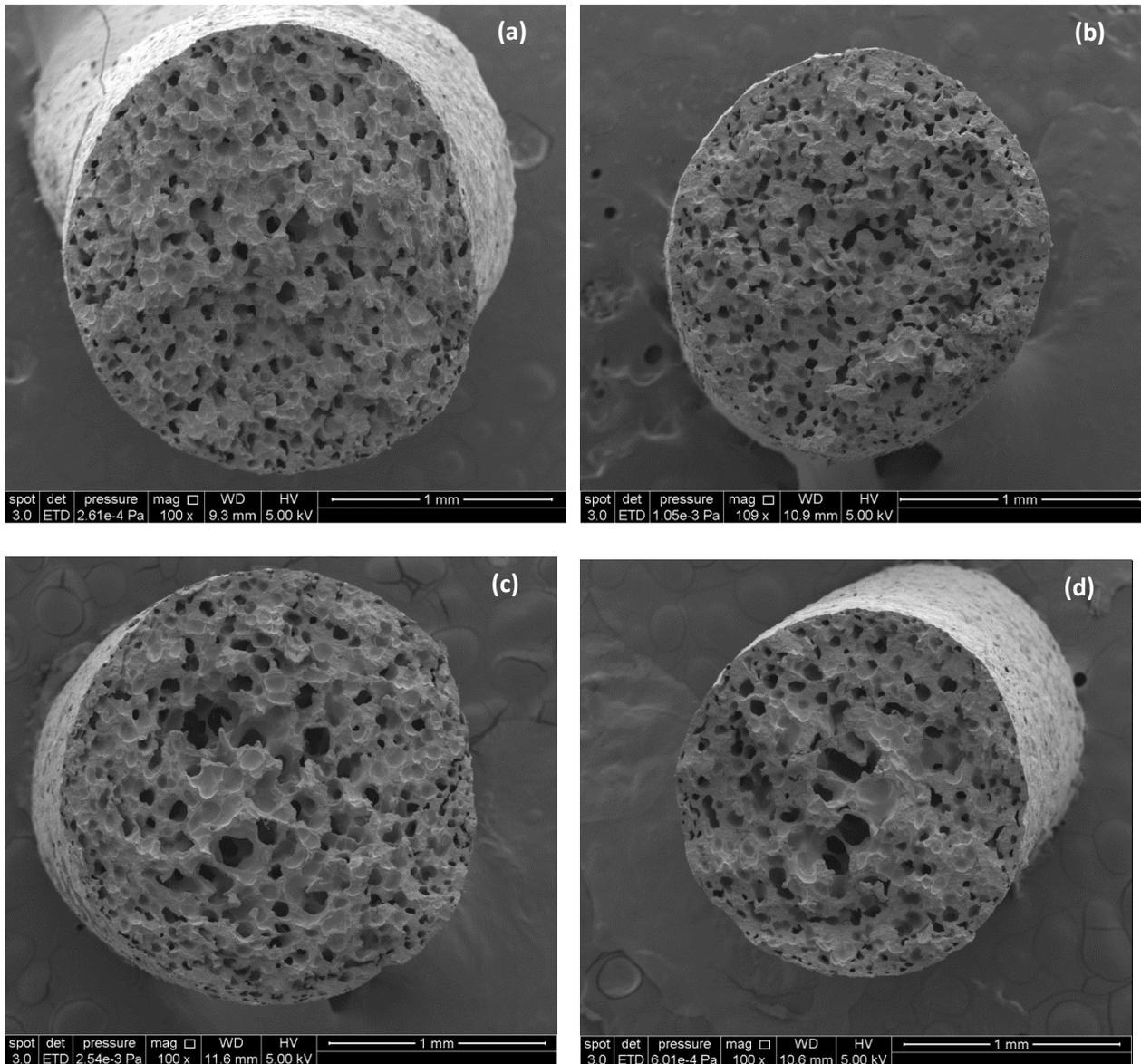


Fig. 3.6 Cell morphology of PLA/TSBP composite foamed at 150 °C with 1 phr CBA at various rotational speed: (a) 40 rpm, (b) 60 rpm, (c) 80 rpm, (d) 100 rpm.

Effects of screw rotation speed on average cell density and void fraction is illustrated in Fig. 3.7. Both cell density and void fraction exhibit a concave shape. An initial increase of processing speed from 40 to 60 rpm led to a decrease of void fraction from 42.8 to 33.9%. Further increase of rotational screw speed resulted in an increase of void fraction. As mentioned above, a lesser degree of CBA decomposition and growth time are achieved at higher rotational screw speed. However, when processing speed increased to 80 and 100 rpm, void fraction increased. This is probably due to the shear thinning nature of polymer melt. Viscosity decreased significantly and hence made the cells expand more easily. Therefore, larger cell size and expansion ratio resulted at processing speed of 80 and 100 rpm.

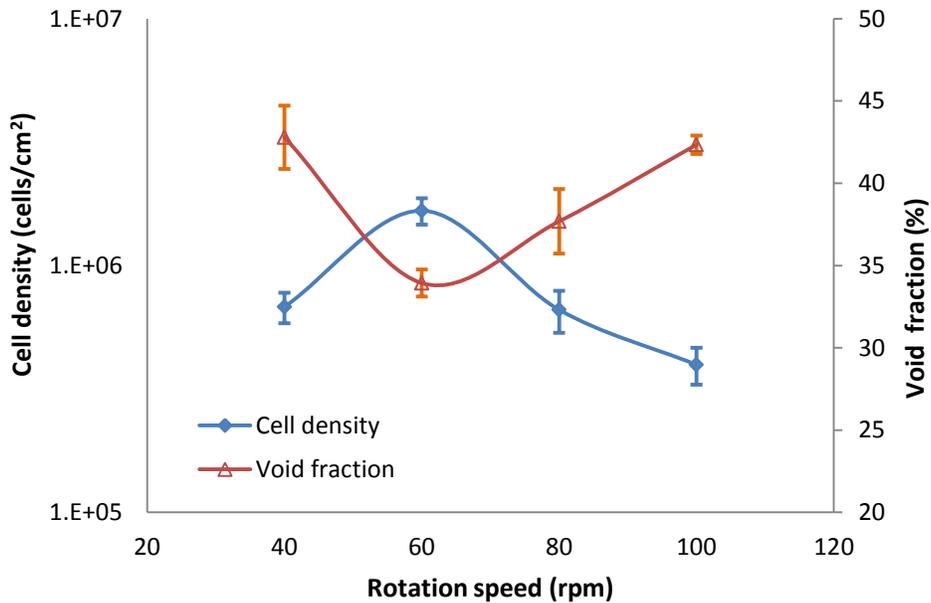


Fig. 3.7 Effect of screw rotation speed on cell density and void fraction of PLA/TSBP composite foamed with 0.5 phr CBA at 150 °C.

Average cell-population density increased from 6.80×10^5 to 1.76×10^6 cells/cm³ when rotational screw speed increased from 40 to 60 rpm as shown in Fig. 3.7. This result is expected because initial increase of rotational screw speed will induce higher pressure drop as shown in Fig. 3.8. According to equation (4)-(6), higher pressure drop will result in lower activation energy and hence faster nucleation rate. However, further increase in rotational speed led to shear thinning of polymer melt. Pressure drop decreased significantly due to reduced viscosity of the polymer melt (Fig. 3.8). The decreased viscosity accelerated thinning of cell walls and consequently the diffusion rate. (Matuana 2008) Coalescence occurred in this case and cell density decreased significantly.

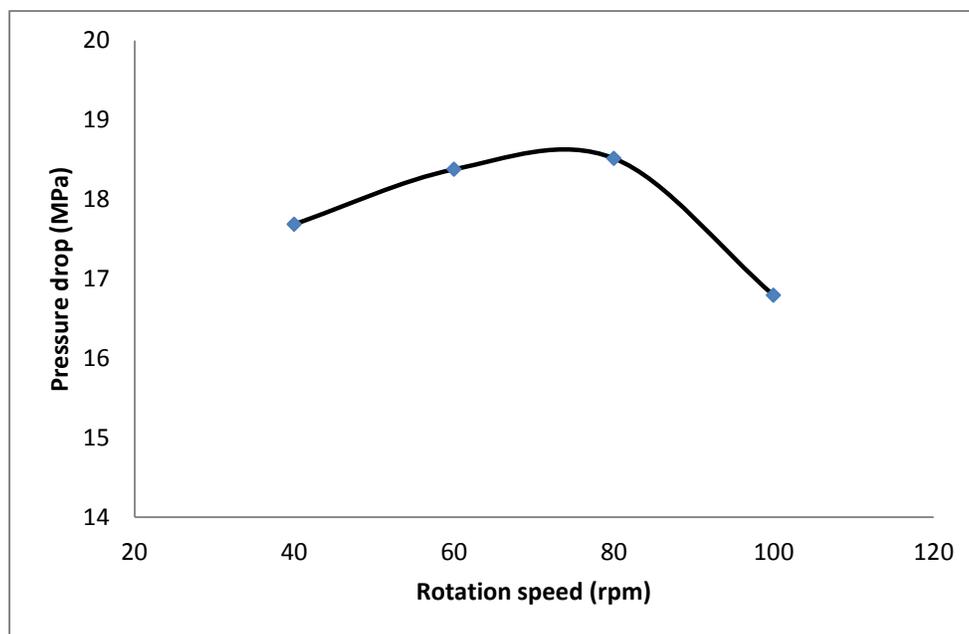


Fig. 3.8 Effect of rotation speed on pressure drop of PLA/TSBP composite.

3.4 Conclusion

A continuous method, extrusion foaming, was employed to foam a PLA/TSBP composite with a chemical blowing agent. Effects of CBA content, foaming temperature and rotational screw speed on cell morphology, average cell-population density and void fraction were investigated. Basically, fine cellular structure is expected in low CBA content, low foaming temperature and moderate processing speed.

Because of low melt strength of PLA, increased amount of CBA content easily resulted in cell coalescence and low average cell density. Early gas escape through the percolated structure of SBP occurred, if excessive amount of CBA content was introduced. In this case, most of the gas escaped instead of blowing the cells, leaving large unfoamed regions.

Temperature is a complex factor: increasing the temperature should have increase the cell density according to classic nucleation theory, but it decreased foaming pressure. Cell nucleation is more sensitive with pressure than temperature on the basis of our discussion.

Rotational speed affects residual time of polymer as well as the foaming agent, so low rotational screw speed led to complete decomposition of CBA and consequently fully grown cells. However, if processing speed was too high, the shear thinning nature of the polymer melt resulted in severe cell coalescence.

Reference

- Afrifah, K. A. and L. M. Matuana (2010). "Impact modification of polylactide with a biodegradable ethylene/acrylate copolymer." Macromolecular Materials and Engineering **295**(9): 802-811.
- Chen, F., L. Liu, et al. (2008). "Performance Enhancement of Poly(lactic acid) and Sugar Beet Pulp Composites by Improving Interfacial Adhesion and Penetration." Industrial & Engineering Chemistry Research **47**(22): 8667-8675.
- Gregorova, A., M. Hrabalova, et al. (2011). "Surface modification of spruce wood flour and effects on the dynamic fragility of PLA/wood composites." Polymer Engineering & Science **51**(1): 143-150.
- Han, X., K. W. Koelling, et al. (2003). "Effect of die temperature on the morphology of microcellular foams." Polymer Engineering & Science **43**(6): 1206-1220.
- Huda, M., A. Mohanty, et al. (2005). "'Green' composites from recycled cellulose and poly(lactic acid): Physico-mechanical and morphological properties evaluation." Journal of materials science **40**(16): 4221-4229.
- Jiang, L., M. P. Wolcott, et al. (2006). "Study of Biodegradable Polylactide/Poly(butylene adipate-co-terephthalate) Blends." Biomacromolecules **7**(1): 199-207.
- Kuboki, T., Y. H. Lee, et al. (2009). "Mechanical properties and foaming behavior of cellulose fiber reinforced high-density polyethylene composites." Polymer Engineering & Science **49**(11): 2179-2188.
- Lee, S. T., C. B. Park, et al. (2007). Polymeric foams: science and technology, CRC.
- Lee, S. T. and N. S. Ramesh (2004). Polymeric foams: mechanisms and materials, CRC.
- Leitner, J., B. Hinterstoisser, et al. (2007). "Sugar beet cellulose nanofibril-reinforced composites." Cellulose **14**(5): 419-425.

- Li, Q. and L. M. Matuana (2003). "Foam extrusion of high density polyethylene/wood-flour composites using chemical foaming agents." Journal of applied polymer science **88**(14): 3139-3150.
- Li, Q. and L. M. Matuana (2003). "Surface of cellulosic materials modified with functionalized polyethylene coupling agents." Journal of applied polymer science **88**(2): 278-286.
- Liu, B., S. Bhaladhare, et al. (2011). "Morphology and Properties of Thermoplastic Sugar Beet Pulp and Poly(butylene adipate-co-terephthalate) Blends." Industrial & Engineering Chemistry Research.
- Liu, B., L. Jiang, et al. (2010). "Synergetic Effect of Dual Compatibilizers on in Situ Formed Poly(Lactic Acid)/Soy Protein Composites." Industrial & Engineering Chemistry Research **49**(14): 6399-6406.
- Liu, B., L. Jiang, et al. (2010). "Study of Effects of Processing Aids on Properties of Poly(lactic acid)/Soy Protein Blends." Journal of Polymers and the Environment **19**(1): 239-247.
- Liu, B., L. Jiang, et al. (2011). "Extrusion Foaming of Poly (lactic acid)/Soy Protein Concentrate Blends." Macromolecular Materials and Engineering **296**(9): 835-842.
- Liu, B., J. Zhang, et al. (2011). "Preparation and Properties of Water and Glycerol-plasticized Sugar Beet Pulp Plastics." Journal of Polymers and the Environment **19**(3): 559-567.
- Manjula Dilkushi Silva, K., K. Tarverdi, et al. (2011). "Incorporation of wheat starch and coupling agents into poly (lactic acid) to develop biodegradable composite." Plastics, Rubber and Composites **40**(1): 17-24.
- Matuana, L. (2008). "Solid state microcellular foamed poly (lactic acid): Morphology and property characterization." Bioresource technology **99**(9): 3643-3650.
- Matuana, L. M. and F. Mengeloglu (2002). "Manufacture of rigid PVC/wood-flour composite foams using moisture contained in wood as foaming agent." Journal of Vinyl and Additive Technology **8**(4): 264-270.

- Matuana, L. M., C. B. Park, et al. (1998). "Cell morphology and property relationships of microcellular foamed pvc/wood-fiber composites." Polymer Engineering & Science **38**(11): 1862-1872.
- Mihai, M., M. A. Huneault, et al. (2007). "Extrusion Foaming of Semi-Crystalline PLA and PLA/Thermoplastic Starch Blends." Macromolecular Bioscience **7**(7): 907-920.
- Stagner, J. and R. Narayan (2011). "Preparation and Properties of Biodegradable Foams." Journal of Polymers and the Environment: 1-9.
- Turquois, T., M. Rinaudo, et al. (1999). "Extraction of highly gelling pectic substances from sugar beet pulp and potato pulp: influence of extrinsic parameters on their gelling properties." Food Hydrocolloids **13**(3): 255-262.
- Zhang, J., L. Jiang, et al. (2006). "Morphology and properties of soy protein and polylactide blends." Biomacromolecules **7**(5): 1551-1561.
- Zhang, J. F. and X. Sun (2007). "Biodegradable foams of poly (lactic acid)/starch. I. Extrusion condition and cellular size distribution." Journal of applied polymer science **106**(2): 857-862.

Chapter 4 Conclusions

In this work, low-cost sugar beet pulp (SBP) was successfully introduced into poly(lactic acid) (PLA) and their low-density foaming application was investigated. The following conclusions can be made:

1. Blending – Novel compatibilizer PBAT-g-MA was introduced and SBP can be processed as thermoplastic.

Traditionally, PLA-g-MA was used as an interfacial modifier to combine PLA with other plastic or filler. In this study, PBAT-g-MA was introduced and proved to be a more effective compatibilizer than PLA-g-MA in terms of tensile properties, i.e. tensile modulus, strength and strain at break. Particle size and shape of SBP was significantly influenced by compatibilizer content. Non compatibilized SBP exhibited big and round shape, but it became too fine and thread shaped when more compatibilizer was added. Improved deformability of SBP indicates better interfacial bonding. SBP can be processed both as a filler component (one-step) and thermoplastic component (two-step) and better performance was achieved when SBP was processed as thermoplastic. DSC results showed that the addition of PBAT as a nucleating agent increased crystallinity of the composite.

2. Foaming – Low density and materials saving foam was achieved through extrusion foaming.

In this study, continuous extrusion foaming of PLA/SBP was successfully achieved. Effects of foaming temperature, the chemical blowing agent (CBA) and rotational screw speed on cell density, void fraction and cellular morphology were investigated. Small cell size is expected at

low CBA content, low foaming temperature and moderate rotational screw speed. Polymer melt and blowing agent would exhibit two phases when too much CBA was added. In this case, the percolated structure of SBP led to early escape of the blowing agent instead of expanding the cell which in turn decreased void fraction significantly. Foaming temperature interplayed with foaming pressure and they are contradictory in their impact on the nucleating rate. However, it turned out that pressure other than temperature is the main factor influencing nucleation rate. High rotational speed was favorable for smaller cell size but it also resulted in shear thinning of polymer melt.