INVESTIGATION OF EFFECT OF PLASTICIZER AND COMPATIBILIZERS ON SOY PROTEIN TERNARY BLENDS

By

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To the Faculty of Washington State University:

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INVESTIGATION OF EFFECT OF PLASTICIZER AND COMPATIBILIZERS ON SOY PROTEIN TERNARY BLENDS

Abstract

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In this research, plasticization and mixing of soy protein concentrate (SPC) with poly (butylene adipate-co-terephthalate) (PBAT) and poly (lactic acid) (PLA) were carried out simultaneously in a single-step compounding process. The effects of plasticizer were investigated. Compatibilizers were found to be indispensible for creating high performance blends and greatly influenced SPC phase morphology in blends. This study investigated the influence of these factors on the phase structure of PLA/PBAT/SPC blends and on the structure-property relationship.

To investigate the plasticization effect on the morphological, tensile and dynamic mechanical properties of PLA/PBAT/SPC composites, acetyl tributyl citrate (ATBC) was added to composites at levels of 0, 3, and 6%. ATBC was found to be effective in

creating PLA/PBAT/SPC composites with good toughness. Elongation of plasticized PLA/PBAT/SPC composites was much higher than that of unplasticized composites. This study also explored fracture morphology through scanning electron microscopy (SEM), indicating a good dispersion of fillers in the polymer matrix. This study also investigated structure-property relationships in detail.

To investigate the compatibilization effect on the morphological, tensile and dynamic mechanical properties of PLA/PBAT/SPC composites, PEOX, PLA-g-MA and PBAT-g-MA were added to the composites at levels of 0, 3, and 6%. The grafting degrees of PLA-g-MA and PBAT-g-MA were 0.75% to 1.18%, respectively. Compatibilizers were found to be indispensable for developing PLA/PBAT/SPC composites with high mechanical and physical properties. The tensile properties of compatibilized PLA/PBAT/SPC composites were higher than those of uncompatibilized ones. Fracture morphology was investigated through scanning electron microscopy (SEM), and indicates enhanced interfacial adhesion. An investigation of dynamic rheology and dynamic mechanical properties also confirmed a percolated network structure.

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Chapter 1 Introduction

Why biomaterials?

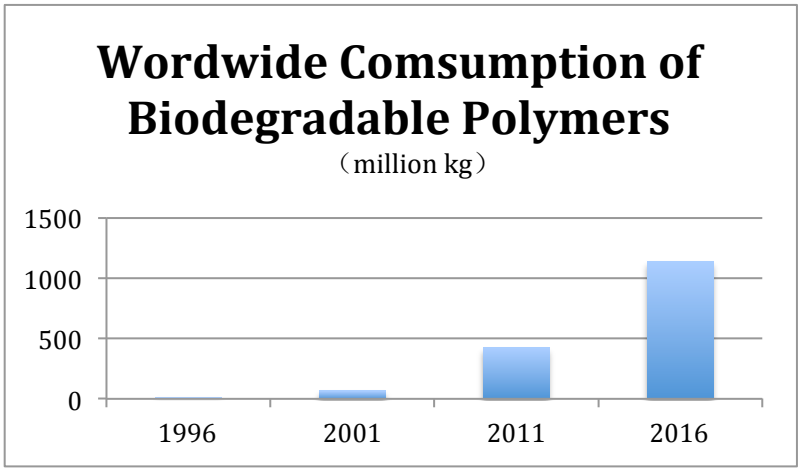
In the past, materials derived from fossil fuels are widely used because their low price and good performance. In the last century, plastics replaced many applications that were once made with metal, due to their low-density, high strength and ability to be easily sharpened. Despite the superior attributes of polymers, polymer pollution poses a serious issue. In an ESI field report, more than 180 species of animals ingest plastic trash. Many news reports have cited a statistic that many polymer products such as ubiquitous receptacles take 500 years to break down in landfills (USATODAY).

To address problem, governments have taken strides to recycle plastics as much as possible. Still, only a small percentage of plastic products used every year can be recycled. Some food packaging, such as fast food containers, along with some types of plastic bags and films are difficult to recycle. Moreover, the increasing cost of waste disposal has also spurred the rising trend to develop alternative materials that replace traditional petroleum-based plastics. For example, the use of biodegradable plastics has increased markedly over the past several years. Global consumption increased from about 14 million kg in 1996 (Gross and Kalra 2002) to 423 million kg in 2011, and is expected to grow by 22% annually in the next 5 years, possibly reaching 1.1 billion kg in 2016 (Chapman 2011). Figure1.1 shows increasing global biodegradable polymer consumption

from 1996 to 2016.

Figure1.1 Worldwide consumption of biodegradable polymers(Gross and Kalra 2002)

(Chapman 2011)



Plant-based bioplastics

Plant-based biodegradable plastic have actually been used for decades. For example, the Ancient Mesoamericans played with rubber balls, invent before 1600 BCE. In modern times, plant-based materials came into commercial use nearly 40 years ago. There are four broad groups of natural plant polymers widely used today (Mooney 2009): rubber, protein, cellulose and starch.

Soy Protein-based bioplastics

Soy protein (SP) can be divided into soy protein isolates, soy protein concentrates and soy flours, depending on the dry weight of protein from high to low.

Table 2 Typical compositions of soy proteins.

Component	Soy flours (%)	Concentrates (%)	Isolates (%)
Protein	56.0	72.0	96.0
Fat	1.0	1.0	0.1
Fiber	3.5	4.5	0.1
Ash	6.0	5.0	3.5
Carbohydrates	33.5	17.5	0.3

Used as simple filler or a stand-alone melt-processable polymer material, SP has many advantages, including low cost and abundance. It can also be melt-processed when sufficiently plasticized, and provides significant tensile strength and stiffness just as plastic materials do. There are four types of plastic materials made with soy protein:

1) Soy protein plastics
2) Soy protein plastics blended with synthetic polymers
3) Soy protein plastics blended with nature polymers
4) Natural fiber-reinforced soy protein composites

When SP alone is used as a plastic material, its strong intra- and intermolecular interaction leads to high viscosity, which must be reduced with a large amount of water

or other processing aids to allow extrusion processing (Zhang et al. 2001). The additional indispensible water also works as plasticizer, which causes SP gelation during the melting process. Other plasticizers such as glycerol (Zhang et al. 2001; Mo and Sun 2002), ethylene glycerol (Wu and Zhang 2001), propylene glycerol (Mo and Sun 2002), 1,2-butanediol (Mo and Sun 2002), 1,3-butanediol (Mo and Sun 2002), polyethylene glycol (Cunningham et al. 2000), sorghum wax (Kim et al. 2003; Lodha and Netravali 2005) and sorbitol (Cho and Rhee 2002; Kim et al. 2003) are also used in the study of soy protein plastics (Mohanty et al. 2005). Moreover, scientists use different plasticizer combinations, such as mixing glycerol with polyethylene glycol, propylene glycol, sorbitol or sucrose with different ratios (Wan et al. 2005) to make soy protein plastic. However, using large amounts of plasticizers often result in low mechanical properties. In addition, reducing agents such as Na_2SO_3 are often used to break up the intramolecular disulfide bonds and keep the chain moving.

Cross-linking agents are another kind of additive for improving mechanical properties, which also significantly enhancest the water resistance of the soy protein plastics. Zinc sulfate (Zhang et al. 2001), epichlorohydrin (Zhang et al. 2001), glutaric dialdehyde (Zhang et al. 2001), formaldehyde (Paetau et al. 1994), acetic anhydride (Paetau et al. 1994) and glyoxal (Paetau et al. 1994) are some cross-linking agents used in soy protein plastics. Although many additives are used in processing SP bioplastics, soy protein plastics are still difficult to process, due to their high viscosity. High moisture sensitivity also limits practical use. In order to overcome these disadvantages, SP is blended with

other thermoplastics.

Many studies have explored the use of commercialized bioplastics blended with soy protein. These biodegradable polymers are often used for their worthy mechanical properties, such as polycaprolactone (PCL) (Zhang et al. 2001), poly (vinyl lactam) (PVL) (Mungara et al. 2002), poly (butylene succinate) (Ki and Ok Park 2001), poly (butylene adipate-*co*-terephthalate) (PBAT) (Chen and Zhang 2009), Poly (vinyl alcohol) (PVA) (Su et al. 2007), poly (lactic acid) (PLA) (Ki and Ok Park 2001; Zhang et al. 2006). In these types of blends, soy protein is usually considered to be filler for reducing the cost of the final product. Commercially available biodegradable synthetic plastics, including PCL, PVL, PBAT and several other polyester amides, usually cost much more than low-grade soy protein such as soy flour and soy protein concentrate (Liu et al. 2002).

Starch (Jane and Wang 1996; Li et al. 2007), cellulose (Wang et al. 2006; Su et al. 2010) and lignin (Huang et al. 2003) are the three main kinds of natural polymers mixed with soy protein plastics. Their superior mechanical properties and structures, which interact with soy protein through hydrogen bonding, cause a marked improvement of tensile strength, modulus and water resistance. However, because starch, cellulose and lignin do not melt during heating, blends made with these materials cannot be developed through common methods such as extrusion or injection molding, which limits their commercial applications.

Another type of plastic made with soy protein is natural fiber-reinforced soy protein composites. Natural fibers provide strength and stiffness to composites. Most natural

fibers are made of lignin and cellulose, with lignin on the surface and cellulose inside. Due to the poor interaction between lignin and soy protein, the lignin on the surface must be removed to expose the finer micro-fiber inside. Alkali is often used to treat the fibers before making composites in order to improve the dispersion of fiber matrix. Moreover, treated fiber contains more hydroxyl groups, leading to a better interaction between the fiber and soy protein matrix. When grass fiber reinforced soy-based bio-composites are treated with alkali, impact strength can be increased about 40% compared to non-treated fiber reinforced composites (Liu et al. 2004).

Although using alkali-treated fiber blends with soy protein plastics will improve mechanical properties, it is difficult to create this type of blend with extrusion and injection molding, because the fiber does not melt during the processing. Therefore, this limits its range of application.

Our previous study on soy protein bioplastics

In our previous studies, PLA and PBAT are all used to modify soy protein plastics.

PLA is linear aliphatic polyester synthesized by poly-condensation of lactic acid or by ring opening polymerization of lactide groups. Usually the raw material can be produced from bacterial fermentation of cornstarch, tapioca products or sugarcanes. Since all the crude materials used to produce PLA come from natural plant material, PLA is an entirely biodegradable and environmental friendly polymer with extensive sources. It can easily degrade to carbon dioxide, water, and humus in an environment with an

appropriate temperature and moisture level, with the addition function of microorganisms.

High strength and high modulus (63 MPa and 3.4 GPa, respectively) gives PLA a wide range of practice. PLA and SP are complementary in many aspects. While PLA provides improved melt processability and water resistance to SP plastics, the use of low grade SP such as soy flour (SF) or SPC reduce costs, improve heat distortion temperature (HDT) and may help accelerate the biodegradation process of the PLA-based plastics. Our recent study demonstrated that PLA blends prepared for SPC containing extra water have much better properties than the blends made from dry SPC in which SPC is merely used as filler (Zhang et al. 2006). When SP containing additional water is melt-mixed with other polymers, it exhibits certain plastic characteristics, like fluidity or deformability. However, the hydrolysis and thermal degradation of PLA can be easily accelerated in the presence of SP, due to various carboxylic or amino functional groups of SP and additional water content. During melt processing, thermal degradation of SP also occurs.

Although this drawback in the melt processability of the blends at high SP loading levels presents a challenge, PLA blends of SP still attract much attention. Since both SP and PLA are rigid polymers, their blends have high strength and modulus. The SP/PLA blends presented great improvement in mechanical properties and water resistance and processability. Poly (2-ethyl-2-oxazoline) (PEOX) has been found to effectively compatibilize this blend system. The blends using SPC demonstrated fine co-continuous

phase structures and superior mechanical properties to those blends using soy protein isolate (SPI). Meanwhile PLA and SPC are all brittle; the blends display brittle properties with very low elongation. For extensive use, these blends need to be toughened.

Blending two polymers to modify the mechanical properties is one of the most inexpensive and common methods to improve industrial applications (Utracki 1990). Most studies have focused on the blending field for toughening polymers. Our previous study explored processing SPC as a plastic component blend with PBAT, along with the mechanical, thermal properties and morphological structures of the resulting blends. PBAT is flexible and tough, but has low strength and modulus, and can be fully biodegradable with the aid of nature enzymes. The elongation of pure PBAT is more than 700%, which make the blends flexible.

Our previous study found that when was mixed PBAT with SPC, the ratio of SPC/PBAT was 50/50 by weight, and the elongation reached 12%. When the SPC was 15%, more than 400% elongation occurred. However, due to PBAT's poor strength and modulus, mechanical properties worsened with higher PBAT contents.

In preparing SPC/PBAT compound, water is often added to SPC prior to compounding as a plasticizer. Water content has a very significant effect on SP plastics, making the SP work as rigid filler to deformable filler from content low to high during the blending (Chen and Zhang 2009; Chen and Zhang 2010). In our previous study, before the last processing step, water was evaporated after compounding; the SPC domains lost its flowability/deformability and behaved like a solid in the subsequent

melting extrusion. Therefore, the blending resulted in the formation of in situ PBAT/SPC composites.

Our current study explored SPC deformability (regulated by water content in SPC), shear force (regulated by PBAT/SPC composition ratio) and compatibilization. The results showed that the deformability of SPC phase in the compounding process was greatly influenced by water content in the pre-compounded SPC. The SPC phase moved from rigid filler to deformable filler by varying the water content in the pre-compounded SPC from 0.6% to 22.5% in SPC/PBAT (30/70, w/w) blend. Moreover, the mechanical interlocking of SPC and PBAT led to improved mechanical properties. We also examined the compatibilization effect in PBAT/SPC blends. The results showed phase structure and mechanical properties of the blends were greatly improved by adding 3% of PBAT-g-MA (Chen and Zhang 2010).

There are still other works related to PLA/PBAT blends, since PLA and PBAT have complementary properties. Blending high strength and modulus brittle PLA with flexible and tough PBAT with poor mechanical properties produces a suitable comprehensive performance. With only 5% of PBAT in the blend, tensile toughness increased greatly and material failure mode changed from brittle fracture of the neat PLA to ductile fracture of the blend. Better still, by adding 15% of PBAT, the stress of the blend was still above 50 MPa while the extension increased to around 170% (Jiang et al. 2006). As from the SEM pictures, in this two-phase system, PBAT was evenly dispersed into PLA matrix around the size of 300 nm, indicating a good phase structure and dispersion.

Problem statement for this SP bioplastics research

Our previous studies showed that SPC/PLA blends demonstrate good water resistance and processing ease. Since both SP and PLA are rigid polymers, their blends show high strength and modulus but have low impact strength. In this study, a third polymer was added to toughen the SPC/PLA blend and developing SP-based plastics. Our previous studies related to PLA/PBAT and SPC/PBAT blends all showed great improvement in their ductility comparing with pure PLA and SPC plastics. So, in this study, PBAT is used to toughen PLA/SPC compound in the ternary polymer blends.

Before this investigation, we studied PLA/PBAT/SPC (50/20/30, w/w/w) blend first. The SPC phase was also pre-compounded with water before compounding. But blend did not show a satisfactory morphology and mechanical properties without any other additives. The strain at break is only 2.5%. We did not see significant improvement in ductility and the blend was still very brittle. This was possibly due to the negative interaction between each surface and intricate structure in the ternary polymer blends. For this, further treatment should be taken to modify the three-component polymer blends.

1 ATBC is used as plasticizer to further improve flexibility.

For the three components are immiscible with each other, especially SPC is hydrophilic and PLA, PBAT are hydrophobic. They do not have good interfacial adhesion. This causes lots of defects in the surface, which will lead to low strain and strength under stretching. To solve this problem, three different kinds of compatibilizers: PEOX,

PLA-g-MA and PBAT-g-MA are used to compatibilize the blends.

Research objectives

Blending SP with other thermoplastics is an economical approach to overcome many problems associated with SP plastics (high viscosity) and reduce the cost of products derived from biobased or biodegradable polymers, such as PLA and PBAT. Although several studies have examined the properties of PLA/SPC, PLA/PBAT and SPC/PBAT blends, no research specified on the three components has explored PLA/PBAT/SPC. We predicted that this blend should have more compromising properties than these binary systems. Recently, multicomponent polymeric blends have emerged as promising new engineering materials. Increasing the number of polymer components in a blend brings more complexity to the polymer material system, and also provides enhanced design flexibility for the control of multiple properties.

In our investigation, the ternary polymer blends faced two main problems, noted above. To address these issues, our study aims to:

1. Identify the plasticizing effect of acetyl tributyl citrate (ATBC) on the properties of the PLA/PBAT/SPC composites.
2. Identify an effective compatibilization method for the preparation of high strength and high modulus PLA/PBAT/SPC composites.

Chapter 2 Effects of plasticizer on the PLA/PBAT/SPC blends

Abstract

Poly (lactic acid) (PLA), poly (butylene adipate-co-terephthalate) (PBAT) and soy protein concentrate (SPC) are all biodegradable polymers. PLA has a high strength and modulus but low elongation. By adding flexible PBAT, toughness was increased. In order to reduce cost, SPC was added to the blend. In this experiment, the ternary polymer composites were prepared with a twin-screw extruder. Acetyl tributyl citrate (ATBC) was used as a plasticizer and poly (2-ethyl-2-oxazoline) (PEOX) was used as compatibilizer. ATBC proved to be an effective plasticizer in this PLA/PBAT/SPC ternary system. Adding 6% of ATBC, elongation increased to be 10 times that of the blend without plasticizer. Scanning electron micrographs revealed improved dispersion of fillers in the PLA matrix. Both dynamic mechanical analysis and differential scanning calorimetry test revealed a large decrease in glass transition temperature of PLA. The decreases in storage modulus and viscosity further convinced a good plasticization effect.

Key word: PLA, PBAT, SPC, plasticizer, compatibilizer

Introduction

As one of the most extensive studied biodegradable polymers, poly(lactic acid) (PLA) has high strength and modulus (63 MPa and 3.4 GPa, respectively), comparable to that of many petroleum-based plastics. Commercial PLA is prepared by either polycondensation of lactic acids or ring-opening polymerization of lactide, which are the cyclic dimers of lactic acids. Currently, lactic acids are mainly produced from fermentation of enzyme-thinned cornstarch. Lactic acid can potentially be produced from many biomass feedstocks, which can be converted to sugars. The abundantly available feedstocks for PLA production make it a promising competitive alternative bioplastics to the ubiquitous petroleum-based materials.

However, comparing to many widely used petroleum-based plastics, PLA is still more expensive. Also, the biodegradation rate of PLA is low because of its hydrophobicity and semi-crystalline structure, which prevent fast water penetration (Kim et al. 2003). For these reasons, we considered blending PLA with the inexpensive nature polymers such as starch, low-grade soy protein like soy meal or soy protein concentrate. PLA blends with natural polymers can reduce the cost of the whole products and increase the biodegradation rate of the composites. Since both PLA and soy protein are rigid polymers, the PLA/SPC blends exhibit high strength and high modulus but low elongation (Liu et al. 2010). Therefore, there is a need to modify the PLA/SPC blends to improve flexibility.

Blending two polymers is the most inexpensive and common way to modified

properties of polymer materials (Utracki 1990). PLA is frequently blended with flexible polymers and elastomers for improved toughness and ductility. Both biodegradable and non-degradable polymers have been used to blend with PLA. To improve toughness and ductility of PLA materials, biodegradable polymer modifiers are preferred because the resulting blends retain the integral biodegradability. Polycaprolactone (PCL) (Simoes et al. 2009), poly (butylene adipate-*co*-terephthalate) (PBAT) (Jiang et al. 2006), poly (butylene succinate) (PBS) (Chen et al. 2005), poly(ethylene oxide) (PEO) (Kim et al. 2001) have been used to blend with PLA to improve flexibility. In general, PLA blends with these polymers exhibited great increase in ductility compared with neat PLA, and many of these blends showed elongation above 100%. However, at the same time, the strength and modulus of such PLA blends exhibited remarkable drops. Among various biodegradable polymer modifiers, PBAT is the most attractive one for its relatively low price compared with that of the others, high effectiveness in flexibilizing PLA and similar hydrophobicity to that of PLA.

Our group has conducted extensive investigations on SPC/PBAT (Chen and Zhang 2009; Chen and Zhang 2010) and PLA/PBAT (Jiang et al. 2006; Chen and Zhang 2009) blends. Since the strain at break of PBAT is above 800%, this flexible component can make the polymer blends change from brittle to ductile, depending on the blend composition. For example, the SPC/PBAT blend containing 50%PBAT showed an elongation of 12%, while the blend containing 70% PBAT exhibited an elongation above 100%. PBAT has been shown to be very effective in flexibilizing PLA. With 20% PBAT,

the PLA/PBAT blend displayed an elongation up to 200%. Promising results for development of flexible PLA and SPC plastics using PBAT prompted us to consider utilizing PBAT to modify the properties of PLA/SPC blends.

Another approach to improve the ductility of PLA/SPC blends is to add plasticizers. Derivatives of Glycerol (Martin and Averous 2001), poly(ethylene-glycol) (PEG) (Jacobsen and Fritz 1999), lactide (Nijenhuis et al. 1996) were used as plasticizers for PLA. There is a growing trend in the use of citrate derivatives, such as tributyl citrate (Ljungberg and Wesslen 2002; Ljungberg et al. 2003; Ljungberg and Wesslen 2003), acetyl triethyl citrate (Ljungberg and Wesslen 2002; Zhang and Sun 2004), and especially acetyl tributyl citrate (ATBC) (Coltelli et al. 2008) to plasticize PLA. Due to their low toxicity, citrate derivatives are widely used in the medical, food and toy industries. Effects of ATBC on the PLA (Kranz et al. 2000; Baiardo et al. 2003) and PLA/PBAT blends have been studied (Coltelli et al. 2008). Addition of 25%ATBC increased the strain at break of PLA 100 times that of pure PLA. ATBC appeared more effective than PBAT on flexibilizing PLA in terms of elongation. The addition PBAT resulted in the toughening of the fragile PLA matrix, but further plasticization with a low ATBC concentration resulted in an improvement in the elongation only in proper composition of PBAT/PLA. The plasticization effect of ATBC seems complicated in the PLA/PBAT blends. Depending on the composition of the blends, for example, for the blend with a PLA/PBAT weight ratio of 80/20, the elongation first decreased and then increased with the addition of ATBC. This reduced toughness from additional plasticizer in some

conditions was mainly due to the decreasing of inter-particle distance between the PBAT domains, caused by the preferential solubilization of ATBC in PBAT (Coltelli et al. 2008). When the PLA/PBAT weight ratio was set at 75/25, the addition of 20% ATBC increased the elongation by three times. Therefore, ATBC as appears to be an effective plasticizer to toughen PLA/PBAT blends. However, no studies have examined the ternary polymer blends comprised SP, PLA and PBAT when using ATBC as plasticizer.

In this study, we added the third polymer PBAT to toughen the polymer blend, but since all three components are immiscible with each other, final results could not be satisfied. Therefore, compatibilizer was added to improve results, which is discussed in the next chapter.

In this investigation, a series of PLA/PBAT/SPC composite were prepared by extrusion with different ratio of ATBC. The content of plasticizer was set as 0, 3 and 6% with or without compatibilizer. The project aims at finding out the effect of ATBC as a plasticizer in PLA/PBAT/SPC composites on mechanical, thermal, thermal dynamic and morphological properties.

Experimental Section:

Materials.

PLA (2002D) was obtained for this study from Nature Works. The physical properties provide by the datasheet shows a specific gravity at 1.24, melt index about 5 to 7 g/10 min. The PBAT (Ecoflex F BX 7011) was purchased from BASF Corp. It has a density

of 1.26 g/cm3 exhibits a weight- average molecular weight of 145 kDa, polydispersity of 2.40 (GPC analysis), and a glass transition temperature and melting point of -29 and 115 °C (dynamic mechanical analysis (DMA) and DSC analysis), respectively. Commercial grade SPC (Arcon F) was acquired from Archer Daniels Midland Company (Decatur, IL). It contends ~69% protein, 20% carbohydrate, 3% fat, and 5% moisture. Citroflex A4 (acetyl tributyl citrate) was provided by Vertellus Performance Material, Inc. PEOX (*M*w 500 kDa) was provided by Aldrich. Sodium sulfite was made by J.T. Baker Chemical Company (Phillips- burg, NJ).

Sample preparation

SPC (100 parts on dry weight) was pre-formulated by mixing with sodium sulfite (0.5 parts) and water (adjusted the moisture content to 5 and 10 parts on SPC dry weight) in a kitchen mixer and equilibrated in sealed plastic bags at room temperature overnight. Accordingly, the preformulated SPC is denoted as SPC-5%H_2O and SPC-10%H_2O, respectively, to indicate the water content. Prior to compounding, the formulated SPC, PLA, PBAT, PEOX and ATBC were manually mixed in a plastic bag and subjected to extrusion compounding. Extrusion compounding was performed using a co-rotating twin-screw extruder (Leistritz ZSE-18HP) equipped with a volumetric feeder and a strand die. The screw diameter was 18 mm, with a length- to-diameter ratio (*L*/*D*) of 40. The extrusion compounding of PLA/SPC blends and PBAB/SPC blends have been extensively studied in our group. Therefore, in this study, the processing conditions for the blend preparation was very similar to that in the compounding of PLA/SPC blends

(Liu et al. 2010). To reduce the hydrolysis of PLA, the extrusion compounding temperature was set as low as possible in our previous study (Zhang et al. 2006). In this study, a similar method was adopted. Extruder temperatures were set at 120, 140, 150, 155, 160, 150, 135 and 125 °C from the first heating zone to die. The screw speed was 60 rpm for all blends. The extruder was vented at the 6th heating zone on the barrel to remove moisture from melt processing. The extruded strands were cooled in a water trough and subsequently cut into pellets. The PLA/PBAT/SPC ratio in the blend was fixed at 50/20/30 (w/w/w). For the convenience of expression, the blend samples were denoted by Wx-PEOXy-ATBCz in which W denoted water and x the content of water on the basis of dry weight of SPC; y and z denoted the content of PEOX and ATBC on the basis of total weight of PLA, SPC (dry weight) and PBAT, respectively. For example, W10-PEOX3-ATBC3 denoted the PLA/PBAT/SPC blend was prepared from the pre-formulated SPC containing 10% water on the dry SPC basis and contained 3 phr PEOX and 3 phr ATBC on the total polymer weight.

Sheet Extrusion.

Blend sheets were extruded from above pellets using a twin-screw extruder (Leistritz ZSE-18HP). Before forming sheets, the compounding pellets were dried in an oven 80°C overnight to dry the pellets, and then extruded using 6-inch die at about the same temperature used in making blend. The temperature profile of the extruder was 120, 140, 150, 155, 160, 160, 150 and 145 °C (feed throat to die). The die temperature was set at 145 °C and water control were set at 40 to 50 °C, depending on different formulations.

Tensile Specimens.

The sheet we made from extrusion is about one millimeter and the standard tensile bars (ASTM D638, Type IV) could be easily cut into shape with Type IV mode under pressing machine (Hydraulic Unit Model #3912).

Formulation.

Table 2.1 gives the formulations of all the blends studied in this work. In fact, all blends had the same polymer component composition, i.e., containing 50% PLA, 30% SPC and 20% PBAT. These blends can be categorized into three groups. Groups I and II were intended to compare the effects of water content in the pre-formulated SPC on the resulting ternary blends, while group II and III were intended to compare the effects of the compatibilizer PEOX on the blends. In each group, the content of ATBC in each sample was varied to compare the effect of TBC concentration on the properties of the resulting blends. A control sample was also provided

Table 2.1 Formulations of PLA/PBAT/SPC blends with control samples[1]

Group	#	Sample code[2]	PLA	PBAT	SPC (dry weight)	PEOX	ATBC	H_2O	Na_2SO_3
I	1	W5-PEOX3-ATBC0	50	20	30	3	0	1.5	0
	2	W5-PEOX3-ATBC3	50	20	30	3	3	1.5	0
	3	W5-PEOX3-ATBC6	50	20	30	3	6	1.5	0
II	4	W10-PEOX3-ATBC0	50	20	30	3	0	3	0.15
	5	W10-PEOX3-ATBC3	50	20	30	3	3	3	0.15
	6	W10-PEOX3-ATBC6	50	20	30	3	6	3	0.15
III	7	W10-ATBC0	50	20	30	0	0	3	0.15
	8	W10-ATBC3	50	20	30	0	3	3	0.15
	9	W10-ATBC6	50	20	30	0	6	3	0.15
	10	PLA[2]	100	0	0	0	0	0	0

[1]All units are in parts.

[2] W denoted water and the number followed the water content (%) in the pre-formulated SPC on the basis of SPC dry weight; the number followed PEOX indicated PEOX content (%) on the basis of total polymer weight; and the number followed ATBC indicated the content (%) of ATBC on the basis of total polymer weigh

Mechanical Testing.

Tensile tests were performed on an 8.9-kN, screw-driven universal testing machine (Instron 4466) equipped with a 10 kN electronic load cell and mechanical grips. The tests were conducted at a crosshead speed of 5 mm/min with strains measured using a 1-inch extensometer. Following ASTM D-638, the samples were conditioned at 23°C and 50% RH for one week before testing. Five replicates were tested for each sample to obtain an average value.

Morphology.

A field Emission Scanning Electron Microscopy (FE SEM, Quanta 200F) was used in this test to investigate the morphological structure of the PLA/PBAT/SPC compound. Tensile fracture surfaces of the composites were examined under the cross direction. The dried surfaces were then sputter-coated with gold prior to examination.

Differential Scanning Calorimetry (DSC).

DSC (TA 2920) was performed to obtain the crystallization behavior used the specimens sliced from the sample sheets. About 6 mg of specimens were crimp-sealed in 40-μL aluminum crucibles. A sealed empty pan was used as a reference. All specimens were scanned from 20 to 180 °C at 10 °C · min^{-1} to get the glass transition temperature and crystallinity of PLA in the PLA/PBAT/SPC composites. Samples were characterized in an inert environment using nitrogen.

Rheology.

Dynamic rheological properties of the PLA/PBAT/SPC blends were assessed using a strain-controlled rheometer (DISCOVERY HR-2). Samples were tested using a parallel-plate geometry (d=25 mm) with a gap distance of 1 mm. The test temperature was set at 165 °C. All the samples were cut from the compounding sheet after conditioning. A strain sweep test was

initially conducted to determine the linear viscoelastic region of the materials. A dynamic frequency sweep test was subsequently performed to determine the dynamic properties of the blends. The strain and frequency range used during testing were 1% and 0.1-500 rad/s, respectively. Steady-state shear tests at the same temperature were also conducted to investigate the viscosity-shear rate relationship.

Dynamic Mechanical Analysis (DMA).

Dynamic mechanical properties of PLA/PBAT/SPC composites and effect of plasticizer were studied by a dynamic mechanical analyzer (DMA, TA Q-800). DMA specimens (1 × 13 × 35mm^3) were cut from extruded sheet samples and tested using a single-cantilever fixture at 1 Hz vibration frequency. All tests were conducted at a strain of 0.03% using a 2 °C · min^{-1} temperature ramp from -50 to 150 °C.

Water Absorption.

According ASTM D570-98, sheet samples were cut into the form of a bar 76.2 mm (3 in.) long by 25.4 mm (1 in.) wide by the thickness of the material. All samples were first dried at 50±3 °C for 24 h and then held in a desiccator until they reached room temperature. Immediately weighed samples were accurate to 0.001 g. Subsequently, the dried samples were placed in distilled water at 23±1 °C for certain intervals, one hour, two-hour, twenty-four hour and forty-eight hour. The samples were then removed from the water, using tissue paper to erase excess surface water, and weighed to 0.001 g accuracy. Five applications were chosen from each formulation. Water absorption was calculated on a dry sample weight basis.

Results and Discussion

Tensile Properties.

Table 2 shows the mechanical properties of different PLA/SPC/PBAT ternary blends. The samples in Table 2 can be classified into three groups. In the first group, the ternary blends were compatibilized with 3% PEOX and prepared from the pre-formulated SPC containing 5% water (SPC-5%H_2O).In the second group, the blends were also compatibilized with 3% PEOX blends, but were prepared from the pre-formulated SPC containing 10% water (SPC-10%H_2O).I In the third group, the blends were prepared from SPC-10%H_2O without compatibilizer. For all three groups of ternary blends, regardless of water content in the pre-formulated SPC and whether PEOX was present, the strain at break of the blends improved significantly with the addition of ATBC. However, the tensile strength and modulus decreased with increasing ATBC content. This result was mainly due to the plasticizing effect of ATBC on the PLA matrix. By varying the ATBC content from 0 to 6%, the polymer blends changed from brittle to tough. For example, in the first group, the strain at break for the blend without ATBC was 5.1% and the strain increased to ~55% for the blend with 6% ATBC.

In this study, blends were prepared from the pre-formulated SPC containing different amounts of water. Water is a widely used plasticizer for soy protein (SP) plastics and is necessary in the preparation of neat SP plastics (Zhang et al. 2001). In our previous studies on SP blends, we found that water in the pre-formulated SPC supported the formation and fine dispersion of elongated SP threads in the matrix polymer (Zhang et al. 2006). The resulting blends showed significantly higher tensile strength and modulus than their counterparts made of dry SPC. In other words, the presence of water in the pre-formulated SPC enabled SPC to behave like a plastic during compounding, i.e. being deformable and forming elongated threads under

shear stress. In contrast, dry SPC behaved like rigid particles during compounding and showed little change in particle shape and size.

However, we also found that water content from 5 to 10% in the pre-formulated SPC had little influences on the tensile strength and modulus of the resulting blends. Even so, the ductility of the blends changed significantly with varying water content. For the blends with PEOX and without ATBC, the blend prepared from SPC-10%H_2O displayed a strain at break of 33.8%, which was much higher than that (5.1%) of its counterpart prepared from SPC-5%H_2O. But when compatibilizer was not used, even though the blend was prepared from SPC-10%H_2O, it still exhibited a brittle behavior with a strain at break of ~2.6%.

In Figure 2.1, the stress versus strain curves show yield points (maximum load) and stable neck growth through cold drawing. The blends without ATBC exhibited the highest stress and lowest elongation among the three curves. With increasing ATBC content, the stress decreased and strain increased dramatically (Coltelli et al. 2008). The elongation rose almost 20 times with the addition of 6% ATBC. The stable neck growth through cold drawing was likely due to the debonding-induced shear yielding of the plasticized composites (Jiang et al. 2006).

Table 2.2 Tensile properties of PLA/PBAT/SPC ternary blends[1]

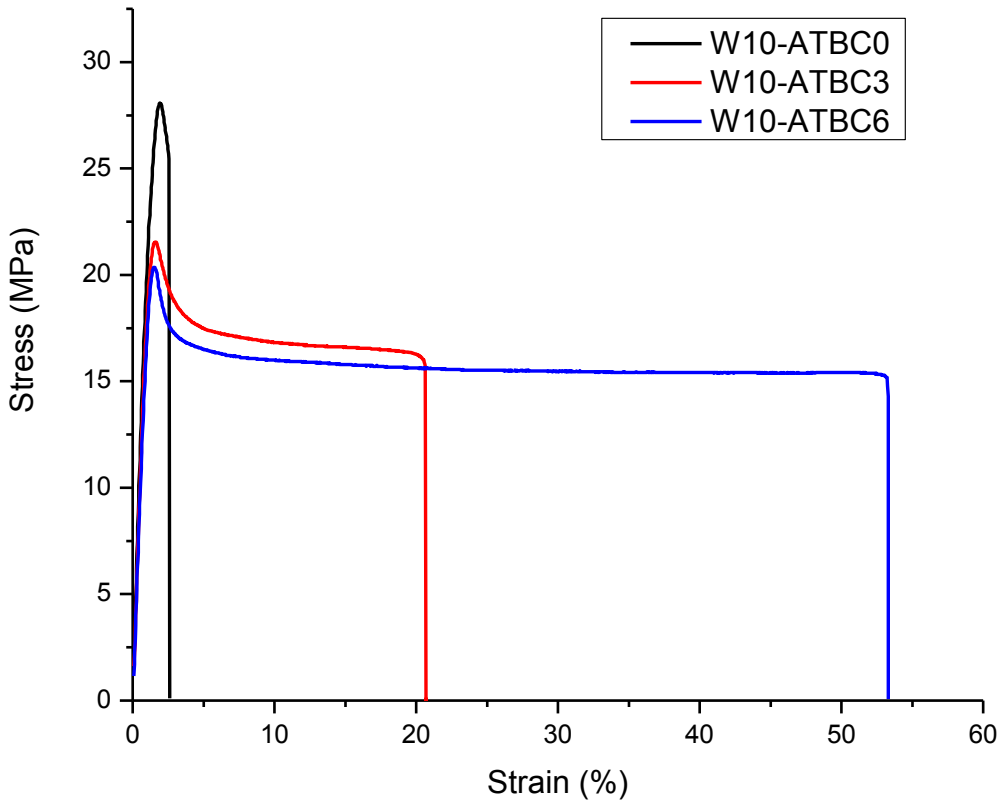
Group	Sample No.[2]	Strength (MPa)	Elongation (%)	Modulus (GPa)
I	W5-PEOX3-ATBC0	28.4±0.3	5.1±1.0	2.41±0.10
	W5-PEOX3-ATBC3	20.8±0.6	29.9±6.7	2.17±0.13
	W5-PEOX3-ATBC6	18.7±1.0	55.2±5.8	1.78±0.19
II	W10-PEOX3-ATBC0	27.6±0.9	33.8±3.3	2.41±0.20
	W10-PEOX3-ATBC3	23.6±1.1	40.0±3.5	2.08±0.16
	W10-PEOX3-ATBC6	18.7±0.9	54.3±2.6	1.73±0.16
III	W10-ATBC0	27.9±0.5	2.6±0.1	2.26±0.03
	W10-ATBC3	21.3±0.2	21.6±0.8	2.30±0.05
	W10-ATBC6	21.0±0.6	51.6±8.1	2.18±0.14
	PLA[3]	64.7±0.7	3.9±0.5	3.49±0.08

[1] The PLA/PBAT/SPC ratio in the blend was fixed at 50:20:30 (w/w/w).

[2] Sample No Wx-PEOXy-ATBCz: W denoted water; x denoted the content of water in the basis of dry weight of SPC; y and z denoted the weight content of PEOX and ATBC in the whole blend respectively.

[3] PLA samples are prepared through injection molding.

Figure 2.1 Stress-strain curves showing the effect of ATBC on the tensile properties.

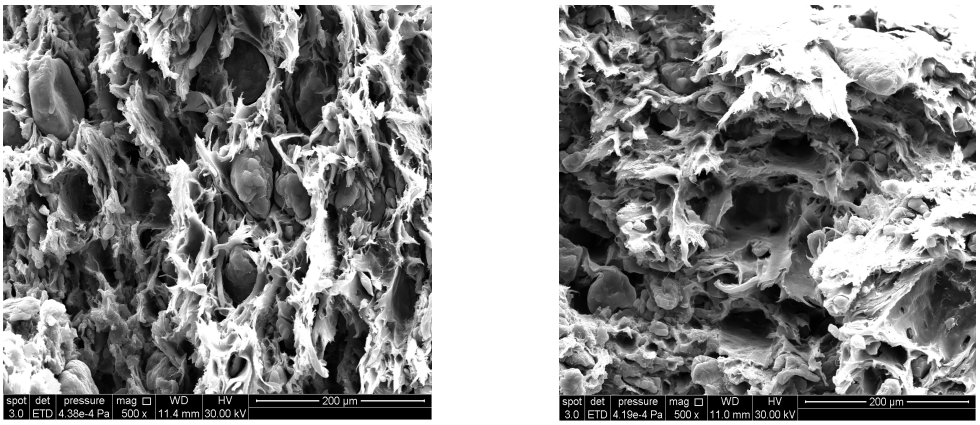


Morphology of tension fracture surfaces

Mechanical properties are strongly determined by the interfacial adhesion and morphology of the polymer blends. Figure 2.2 shows the SEM images of the tensile fracture surfaces. Without ATBC, large SPC particles were clearly noted on the fracture surface. Addition of ATBC in the blends clearly resulted in fine dispersion of the particles in the PLA matrix, which suggests that interfacial adhesion between SPC and PLA was greatly improved with the addition of ATBC. Because ATBC is a good plasticizer for PLA, one likely reason for the improved interfacial adhesion was that some ATBC was also dissolved in SPC. There is a portion of hydrophobic

segments in soy protein molecules which enables it to absorb a certain amount of hydrophobic ATBC. If this did occur during compound processing, the surface properties of SPC would be definitely altered and hence its interfacial tension with the PLA phase.

Figure 2.2 Representative SEM micrographs of tensile fracture surfaces of PLA/PBAT/SPC (50/20/30 w/w/w water is set to 10% in SPC) composites.



(a) PEOX3ATBC0 (b) PEOX3ATBC6

DSC results

Fig. 2.3 shows the DSC thermograms of extruded sheet samples of PLA/PBAT/SPC ternary blends with different ATBC contents. The thermograms from the first heating scan revealed the glass transition temperatures and crystalline status of the samples. The glass transition temperature (T_g), enthalpy and the degree of crystallization are summarized in Table 2.3. The ternary blend without plasticizer had a T_g of ~59.2 °C. The addition of ATBC in the compound resulted in decrease in the T_g of PLA. The T_g decreased to 49.6 and 42.4 °C with 3 or 6% of ATBC, respectively. At the same time, decreasing the cold crystallization temperature of PLA also decreased with ATBC. This was mainly due to increased mobility of PLA with plasticizer,

which enabled the cold cryatillization of PLA to proceed at lower temperatures. The melting temperature of PLA decreased from158.2 °C for the blend without ATBC to 154.8 °C for the blend with 6% ATBC.

Without plasticizer, the crystallinity of the PLA in the ternary blend with 3 phr of PEOX was only about 3.5%. This indicates that the extruded samples were almost amorphous. Our previous studies produced similar results (Jiang et al. 2006; Zhang et al. 2006; Chen et al. 2008). Although PLA is a semi-crystalline polymer, it usually crystallizes slowly, and the injection-molded PLA products do not have a high crystallinity. Usually, nucleating agent or post process annealing is needed to increase crystallinity. With increasing content of ATBC from 0 to 6%, the crystallinity of the PLA slightly increased from 3.5 to 4.9%, which was mainly caused by the increasing mobility of PLA.

Table 2.3 First heating scans of DSC results of the PLA/PBAT/SPC composites with different content of ATBC.

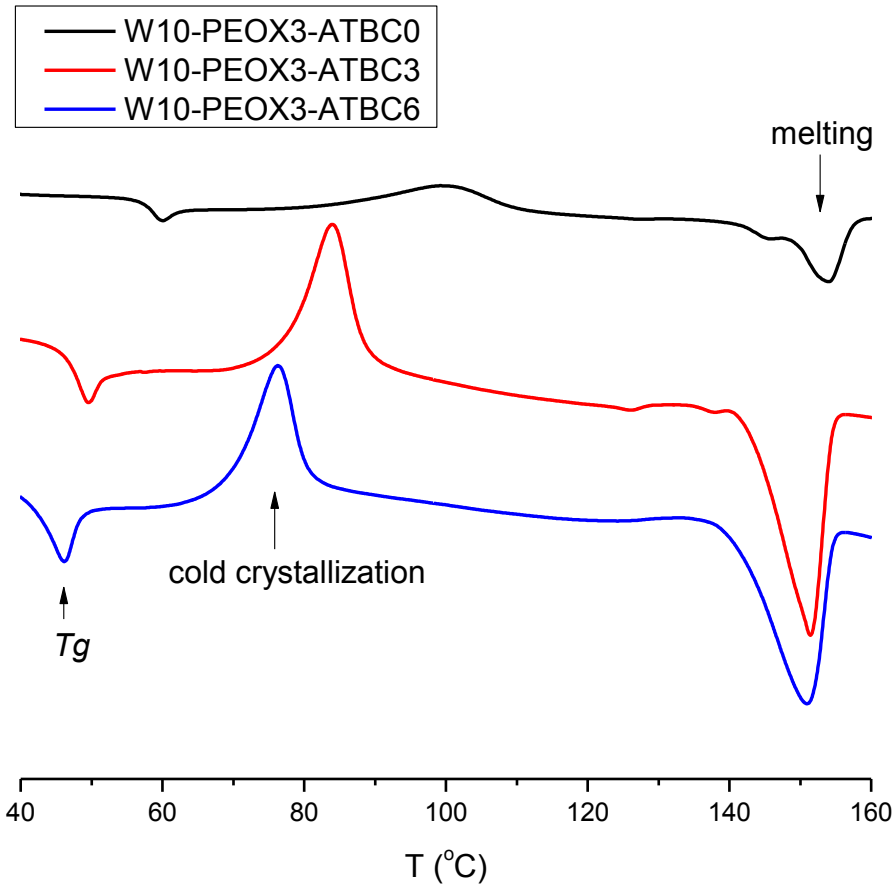
Sample	T_g(°C)	Cold crystalization		Melting		Crystallinity (%)[2]
		T_{cc}(°C)	ΔH_{cc}(J/g)[a]	T_m(°C)	ΔH_m(J/g)[1]	
W10-PEOX3-ATBC0	59.2	105.7	11.2	158.2	14.2	3.5
W10-PEOX3-ATBC3	49.6	90.8	10.5	156.2	14.0	4.1
W10-PEOX3-ATBC6	42.4	82.3	10.2	154.8	14.4	4.9

[1] Data corrected for the percentage of PLA in the blend.

[1] The heat of fusion of 100% crystalline PLA is 86J/g(Chen et al. 2009).

2 Crystallinity= $\frac{\Delta H_m - \Delta H_{cc}}{\Delta H_{PLA}} \times 100\%$.

Figure 2.3 Melting curve of PLA/PBAT/SPC blends of the first scan. Heating rate=10°C · min^{-1}



Rheological properties.

Dynamic rheological measurement is a sensitive method in characterizing the morphological structure of polymer blends and composites because the structure of polymer materials is reserved under small strain test condition(Utracki 1990). The polymer matrix and fillers, especially the state of dispersion of its fillers strongly affects the rheological properties (Macosko and Larson 1994; Zhang et al. 2006; Liu et al. 2007). In order to detect microstructural features, dynamic rheology under oscillatory shear is preferred (Macosko and Larson 1994). Figure 2.4 shows the storage modulus (G′), loss modulus (G″) and complex viscosity ($\eta*$) of the ternary polymer blends and pure PLA.

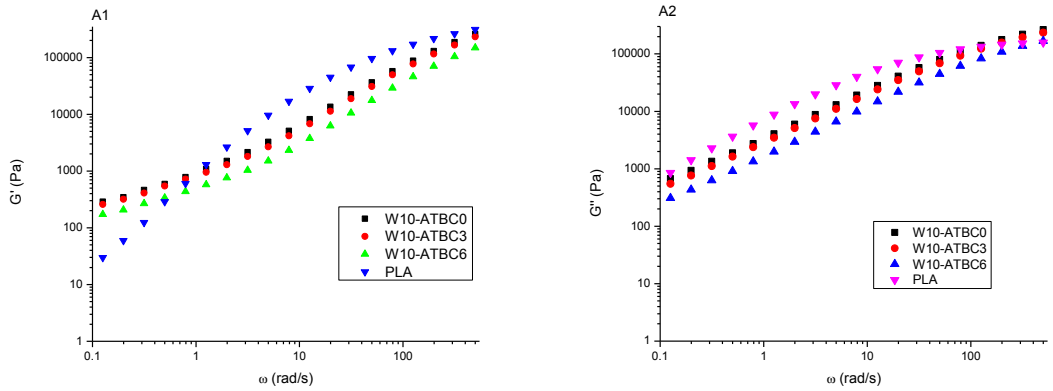
PLA displayed a terminal behavior ($G' \propto \omega^{1.54}$ and $G'' \propto \omega^{0.90}$), which was close to the theoretical prediction ($G' \propto \omega^2$ and $G'' \propto \omega$) for a typical narrow molecular weight distribution linear polymer. However, additions of PBAT and SPC dramatically increased G′ and G″ in the low frequency range. On the contrary, the G′ of pure PLA was higher than that of the ternary blends in the high frequency zone which contained ATBC blends, and showed more shear thinning behavior. In Table 2.4, as ATBC content increased from 0 to 6%, G′ lessened in the whole frequency range and in the terminal zone, while the slopes (n, scaling exponent) of *log(G')* vs. *log(ω)* in group 2 and group 3 changed from 0.77 to 0.64 and from 0.72 to 0.64, respectively.

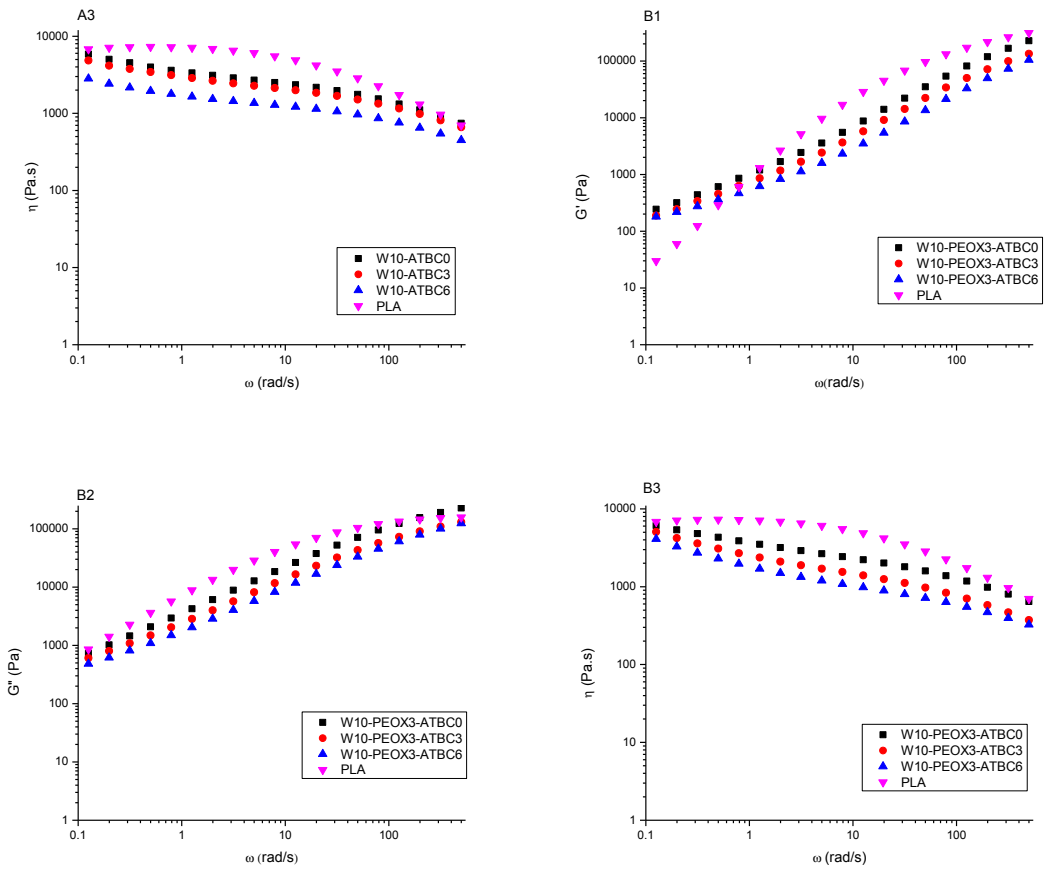
Furthermore, the decreased melt elasticity of the blends was also reflected in the influence of ATBC on complex viscosity $\eta*$. Compared with the $\eta*$without ATBC, a general increase in $\eta*$ of the blends was noted in the whole frequency range. In the terminal zone, the plot of $(\eta*)$ vs. (ω) for the neat PLA shows a Newtonian (primary) plateau. For the blends, we could not see any Newtonian plateau, and the melt displayed a significant shear-thinning behavior over the whole frequency range. This reduced complex viscosity with additional ATBC content reveals a better dispersion of fillers.

Table 2.4 Slopes in the terminal zone

Group	Sample No.	Slopes in the terminal zone	
		$\log(G')/\log(\omega)$	$\log(G'')/\log(\omega)$
2	W10-PEOX3-ATBC0	0.77	0.79
	W10-PEOX3-ATBC3	0.72	0.73
	W10-PEOX3-ATBC6	0.64	0.71
3	W10-ATBC0	0.72	0.82
	W10-ATBC3	0.68	0.83
	W10-ATBC6	0.64	0.85
	PLA	1.54	0.90

Figure 2.4 Dynamic frequency sweeps of PLA/PBAT/SPC blends. Strain=1% and T=165℃.





A1, A2, A3: blends with different content of ATBC without PEOX

B1, B2, B3: blends with different content of ATBC with 3 % of PEOX

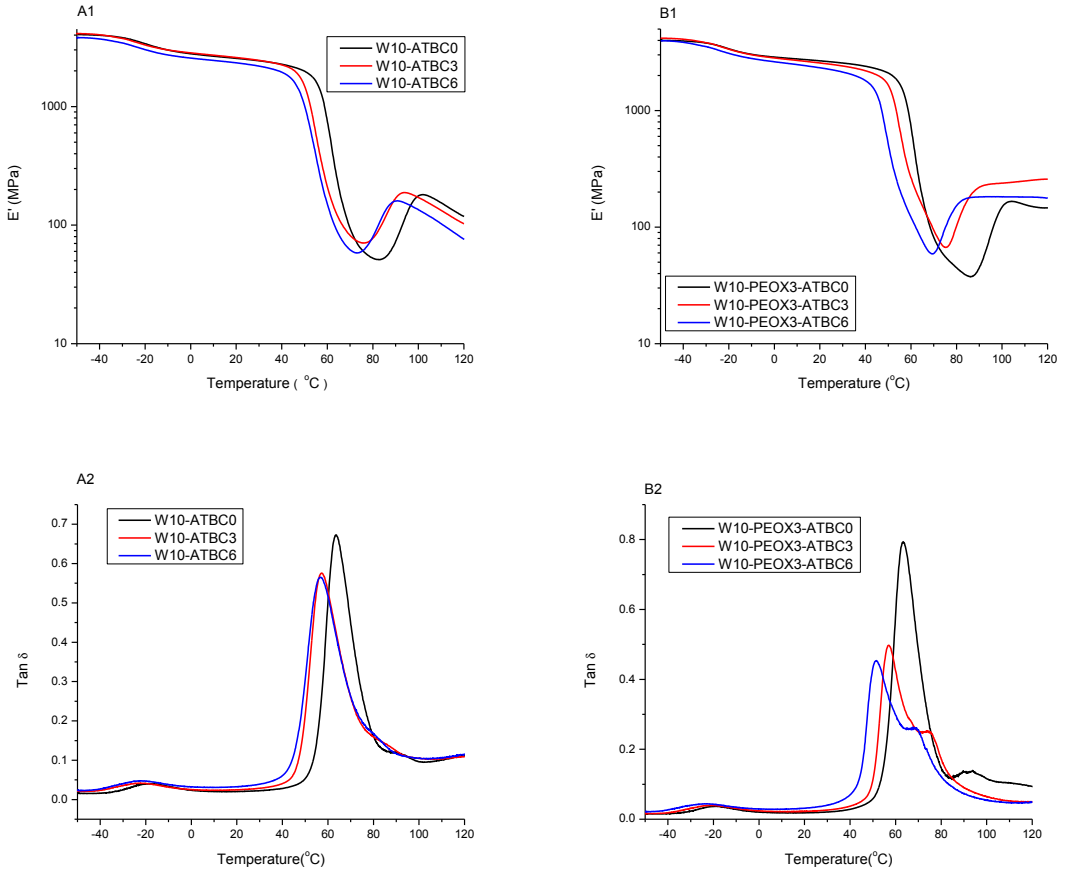
Dynamic Mechanical Properties

Figure 2.5 shows the changes of storage moduli (E') and damping properties of PLA/PBAT/SPC blends with temperature. All samples exhibited a slight decrease in modulus at about -20 °C which corresponded to the T_g of PBAT and a sharp decrease in modulus at about 60 °C, which corresponded to the T_g of PLA (Jiang et al. 2006). Because PBAT was a minor component in the blends and was dispersed in the PLA matrix, the decrease in the modulus experienced by the blends at the T_g of PBAT was much smaller than that at the T_g of PLA.

Modulus recovered to a significant degree when temperature increased to ~90 °C, due to cold crystallization in the PLA. The moduli of the samples at 25, 60 and 120°C are given in the Table 2.5. The data shows that adding ATBC remarkably decreased *E'* due to a plasticizing effect. The blends without ATBC displayed the highest *E'* among the group at all three temperatures.

There was a peak in the damping curves corresponding to each aforementioned drop in *E′*. The peak temperature was determined, and was assumed to be the T_g of each individual component polymer. It is clearly noted that the T_gs of both PBAT and PLA shifted left to lower temperatures as ATBC was added to the blends. Furthermore, the suppression of T_g became more extreme with increasing ATBC content. This result indicates that ATBC plasticized both PLA and PBAT. In addition, there was a peak around 90°Cin the damping curve for the blend W10-PEOX3-ATBC0. A similar peak was not found in the damping curve of the counterpart blend without PEOX. According to our previous study (Zhang et al. 2006), this peak was attributed to the SPC/PEOX mixture. PEOX is miscible with soy protein, and can form a single phase with SPC. The T_g of soy protein is ~160 *°C*. Because PEOX has a low T_g of ~67 °C, the miscible mixture of SPC/PEOX exhibited a reduced T_g. It should be noted that residual moisture in the blend mostly occurred during the SPC phase, which could have further depressed the T_g in this phase. Apparently, the T_g of this phase also decreased as ATBC was added, suggesting that ATBC also had a plasticizing effect on SPC. The *E′* of blends without PEOX started to decrease after the cold crystallization of PLA, while the *E′* of the blends with PEOX remained almost constant from 90 to 120 *°C*. This was probably due to the formation of percolated network structure in the latter case. In addition, the lower damping peaks for the compatibilized blends containing ATBC reflected a good dispersion of particles and the formation of a possible network structure in the matrix.

Figure 2.5 Effect of ATBC on dynamic mechanical properties of PLA/PBAT/SPC (50/20/30) blends.



A1, A2: blends with different content of ATBC without PEOX

B1, B2: blends with different content of ATBC with 3 % of PEOX

Table 2.5 storage moduli in different temperature and glass transition temperature of PLA/PBAT/SPC blends

Group	Sample	*E'* (MPa)			T_g(℃)		
		25°C	60°C	120°C	1	2	3
2	W10-PEOX3-ATBC0	2617	714	258	-19.1	62.9	93.7
	W10-PEOX3-ATBC3	2489	262	177	-21.6	56.1	72.1
	W10-PEOX3-ATBC6	2241	121	146	-23.9	50.1	65.8
3	W10-ATBC0	2493	737	118	-20.6	62.5	/[1]
	W10-ATBC3	2423	211	103	-24.3	55.8	/
	W10-ATBC6	2268	147	76	-24.6	54.9	/

[1] means no third *Tg* shown here.

Water absorption

The blends of hydrophobic PLA and PBAT with hydrophilic SPC displayed increasing water absorption with time, and reached saturation in several weeks. In Table2.6, the ternary polymer blends without plasticizer showed a low water uptake of 1.7% in one hour. With additional ATBC, the water absorption of the PLA/PBAT/SPC blends increased. Since soy protein is highly hydrophilic because of polar functional groups such as amide, amino and hydroxyl groups, neat soy protein plastics often have poor water resistance. In our PLA/PBAT/SPC blends, the water absorption results suggest that the ternary blends had a fairly good water resistance for short periods of immersion such as one or two hours. For a 24 hour immersion in water, the blends also demonstrated low water absorption. This low water absorption was mainly due to the existence of PLA and PBAT content. Pure PLA has ~ 0.8% water uptake at equilibrium (Liu et

al. 2010). ATBC is insoluble in water and creates little water uptake in the polymer sheet (Lin et al. 2000).

Table 2.6 water absorption of the ternary blends.

Sample No.	Water absorption (%)			
	1 hour	2 hours	24 hours	48 hours
W10-ATBC0	1.67±0.11	2.25±0.03	6.63±0.22	9.70±0.15
W10-ATBC3	1.98±0.11	2.60±0.88	7.75±0.03	11.05±0.27
W10-ATBC6	1.74±0.20	2.49±0.23	6.77±0.30	9.45±0.30

Conclusions

PBAT is added into the PLA/SPC binary system to flexibilize/toughen the blends. Addition of ATBC as plasticizer has been shown to be an effective way to further toughen PLA/PBAT/SPC blends. In this study, PLA/PBAT/SPC ternary blends of different compositions were melt-compounded by twin-screw extrusion. Sheet extrusion of these compounds was performed on the same extruder using a 1.5 inch wide die. Test specimens were cut from the extruded sheets. ATBC proved to be very effective in plasticizing PLA/PBAT/SPC blends. This plasticizer significantly enhanced flexibility, especially the elongation. Dispersion also improved with the addition of ATBC, and phase structure became finer. Moreover, complex viscosity was greatly reduced, which is very important in commercial processes since high viscosity will make the presessing difficult. Consequently, ATBC introduced a significant improvement in this

polymer blends.

Chapter 3 Effects of compatibilization on the mechanical and morphological properties of PLA/PBAT/SPC composites

Abstract

In this investigation, poly (lactic acid) (PLA)/ poly (butylene adipate-co-terephthalate) (PBAT)/soy protein concentrate (SPC) blends were melt-compounded in a co-rotating twin-screw extruder. Poly (2-ethyl-2-oxaline) (PEOX), maleic anhydride (MA) grafted PBAT (PBAT-g-MA) and MA grafted PLA (PLA-g-MA) were used as compatibilizer of the PLA/PBAT/SPC composites. This study evaluated the effects of compatibilization on the morphological, tensile and dynamic mechanical properties of the polymer blend.

Keywords: soy protein based composite, ternary polymer blends, compatibilizer

Introduction

In recent years, biodegradable and biobased polymers have received extensive interest for plastic applications as an alternative to conventional petroleum-based plastics. The most common biodegradable synthetic polymers include aliphatic polyesters such as poly (glycolic acids) (PGA), poly (lactic acid) (PLA), polycaprolactone (PCL), polyhydroxybutyrate (PHB) and poly (hydroxybutyrate-co-hydroxyvalerate) (PHBV) (Ke and Sun 2000). Among these types, PLA is the most promising bio-based polymer that is commercially available. PLA exhibits high tensile strength and modulus, which are comparable to those of standard polystyrene. In addition, its biodegradable and compostable characters also make PLA attractive for disposable plastic products. However, the elongation and impact strength of PLA is very low (Hiljanen-Vainio et al. 1996; Rasal and Hirt 2008) and this will make the material easy to break. Also, the price is still high compared with many petroleum-based commodity plastics. Therefore, soy protein concentrate (SPC) is often used to reduce costs. Since both PLA and SPC are rigid, the PLA/SPC binary blends must be toughened in order for them to form superior products for industrial and commercial use.

Polymer blending is a cost-effective way to modify the properties of plastics. Many studies of PLA/PBAT (Jiang et al. 2006) and SPC/PBAT (Chen and Zhang 2009; Chen and Zhang 2010) blends have been conducted, showing that blending PBAT with PLA or SPC is an effective method for toughening these plastics. In this investigation, we explore further methods of toughening PLA/SPC blends with PBAT. These PLA/PBAT/SPC ternary blends were further toughened with acetyl tributyl citrate (ATBC). The previous chapter described the plasticizing effect of ATBC in the PLA/PBAT/SPC blends.

Since these three components are immiscible with each other, the poor interfacial bonding

between components reduces their mechanical properties. Especially because PLA, PBAT has very different hydrophilicity than SPC, the interfacial bonding between PLA and SPC, PBAT and SPC is fairly weak, respectively. To solve this problem, we employed several kinds of compatibilizers to improve the compatibility of these materials.

Our previous studies have indicated the existence of poor interfacial adhesion in each of the PLA/PBAT, PLA/SPC and PBAT/SPC binary systems when an appropriate compatibilizer is not present. Interfacial modifiers containing reactive functional groups can generate in situ formed blocks or grafted copolymers at the interface to improve the compatibilization. Methylene diphenyl diisocyanate (MDI) (Zhong and Sun 2001; Huang et al. 2004), polymeric methylene diphenyl diisocyantate (pMDI) (Liu et al. 2010; ZHU 2011; Zhu et al. 2012), poly(2-ethyl-2-oxazoline) (PEOX) (Zhang et al. 2006; Liu et al. 2010), polyvinyllactam (Mungara et al. 2002), glycerol (Graiver et al. 2004; Su et al. 2007), and some other materials have been studied as compatibilizer in polyester and natural polymer blends. In our previous work on PLA/SPC blends, we found that PEOX had a good affinity with SPC (Zhang et al. 2001) (Zhang et al. 2006; Liu et al. 2010), leading to fine phase morphology and substantially improving the mechanical properties of the material. The subsequent addition of pMDI to the PEOX compatibilized PLA/SPC system enable the formation of strong interfacial bonding between PLA and SPC. The increased tensile strength of PLA/SPC was even higher than that of pure PLA. PEOX and pMDI exhibited a significant synergistic effect on the PLA/SPC composite. However, the high reactivity of pMDI with water demands thorough drying of SPC before compounding, so that the SPC component can only work as filler. Moreover, pMDI is considered to be an environmentally hazardous material, making it unsuitable for food packaging or related applications (Zhang and Sun 2004). Recent studies provide a more promising interfacial

modification route, such as grafting a reactive moiety onto the polymer matrix to create a reaction with the natural polymers. PLA-g-MA has been confirmed as an effective compatibilizer in PLA/SP composites (Zhu et al. 2012). Our previous work also indicates that PBAT-g-MA can improve phase structure and create good mechanical properties in PBAT/SPC blends (Chen and Zhang 2010). However, no research has explored the use of PEOX, PLA-g-MA, and PBAT-g-MA as compatibilizer in PLA/PBAT/SPC composites. Thus, our present work fills an important gap in the literature on this topic.

In this study, different contents of PEOX, PLA-g-MA and PBAT-g-MA were used in the blend to investigate its effects on tensile properties, dynamic mechanical properties, crystallization and water resistance of the composites. This work focuses on further improving the phase structure and properties of the PLA/PBAT/SPC composites.

Experimental

Materials.

SPC (Arcon F) was provided by by Archer Daniels Midland Company (Decatur, IL), and contained ca. 69% protein (on dry weight basis), 20% carbohydrate, 3% fat, 6% moisture and a small amount of ash. Nature Work's PLA (2002D) and BASF's PBAT (Ecoflex F BX 7011) were also used as main components in this work. Sodium sulfite was made by J.T. Baker Chemical Company (Phillips- burg, NJ). Other additives such as PEOX (Mw500 kDa) were acquired from Aldrich. ATBC (Citroflex A4) was provided by Vertellus Performance Material, Inc. Maleic anhydride (MA) (95%) and 2,5-Dimethyl-2, 5-di-(tert-butylperoxy) hexane (L101) were purchased from Sigma-Aldrich Chemical Company. MA grafted PBAT (MA-g-PBAT) was prepared by reactive extrusion using L101 as initiator, styrene as co-monomer and the residual

MA was removed under high vacuum at 80 °C. The degree of grafting was 1.18 wt% as determined by titration methods (Chen and Zhang 2009; ZHU 2011). PLA-g-MA was provided by our colleague (Rui)'s former work. Finally, the degree of grafting was 0.75wt%.

Sample preparation.

Before extrusion, SPC (100 parts, dry weight) was pre-formulated by mixing it with sodium sulfite (0.5 parts) and water (adjusted the moisture content to 10 parts) in a kitchen mixer. This mixture was equilibrated in sealed plastic bags at room temperature overnight. Prior to compounding, the formulated SPC, PLA, PBAT, ATBC and compatibilizer were manually mixed in a plastic bag and subjected to extrusion compounding. Extrusion compounding was performed using a co-rotating twin-screw extruder (Leistritz ZSE-18HP) equipped with a volumetric feeder and a strand die. The screw diameter was 18 mm and the length-to-diameter ratio (*L*/*D*) was 40.

Our research group has extensively studied the extrusion compounding of PLA/SPC blends and PBAB/SPC blends in the past. Therefore, we created processing conditions for the blend preparation that were very similar to those used previously for compounding PLA/SPC blends (Liu et al. 2010). To reduce the hydrolysis of PLA, our former work often set the extrusion temperature as low as possible (Zhang et al. 2006). In the current study, the extruder temperatures were set at 120, 140, 150, 155, 160, 150, 135 and 125 °C from the first heating zone to die. The screw speed was 60 rpm for all blends. The extruder was vented at the 6th heating zone on the barrel to remove moisture from melt processing. The extruded strands were cooled in a water trough and subsequently cut into pellets. The PLA/PBAT/SPC ratio in the blend was fixed at 50:20:30 (w/w/w). For the convenience of expression, the blend samples are denoted by PEOXx; PLA-g-MAy; PBAT-g-MAz respectively, in which x, y and z denote the content of

PEOX, PLA-g-MA and PBAT-g-MA in the whole blend, respectively. For example, PEOX3 denotes the PLA/PBAT/SPC blend containing 3 phr PEOX and 3 phr ATBC of the whole polymer blend. Three phr ATBC was added to all formulations.

Sheet Extrusion.

PLA/PBAT/SPC blends sheets were extruded from the above pellets using a twin-screw extruder (Leistritz ZSE-18HP). Compounding pellets were heated in an oven at about 80°C overnight to remove extra water. Then the pallets were extruded with a 6-inch die at about the similar temperature used in making the blend. The temperature profile of the extruder was 120, 140, 150, 155, 160, 160, 150 and 145 $°C$ (feed throat to die). The die temperature was set at 145 $°C$ and the water controls were set at 40 to 50°C, depending on the formulation being tested.

Tensile Specimens.

Sheets were formed from extrusion at about 1mm. The standard tensile bars (ASTM D638, Type IV) could be easily cut into shape with a Type IV mode under a pressing machine (Hydraulic Unit Model #3912).

Formulation.

Table 3.1 shows the formulation of all samples. 10phr water content is based on SPC dry weight. PEOX, PLA-g-MA, PBAT-g-MA and ATBC contents are all based on the whole blend. Data on the control sample is also shown.

Table 3.3 Formulations of PLA/PBAT/SPC blends with control samples.[1]

Sample code	PLA	PBAT	Prepared SPC (dry weight)	Water content	ATBC	PEOX	PLA-g-MA	PBAT-g-MA
Control	50	20	30	3	3	0	0	0
PEOX3	50	20	30	3	3	3	0	0
PEOX6	50	20	30	3	3	6	0	0
PLA-g-MA3	50	20	30	3	3	0	3	0
PLA-g-MA6	50	20	30	3	3	0	6	0
PBAT-g-MA3	50	20	30	3	3	0	0	3
PBAT-g-MA6	50	20	30	3	3	0	0	6

[1]All units are in parts

Mechanical Testing.

Tensile testing was performed on an 8.9-kN, screw-driven universal testing machine (Instron 4466) equipped with a 10 kN electronic load cell and mechanical grips. The tests were conducted at a crosshead speed of 5 mm/min, with strains measured using a 1 inch extensometer. According to ASTM D-638, samples were kept in a conditioned room (temperature 23°C, humidity 50%) for one week before testing, as noted in ASTM D-638. Five replicates were tested for each sample to obtain average values.

Morphology.

Scanning electron microscopy (SEM) was used in this test to investigate the morphological structure of the PLA/PBAT/SPC compound. Tensile fracture surfaces of the composites were examined under the cross direction. The dried surfaces were then sputter-coated with gold prior to examination.

Differential Scanning Calorimetry (DSC).

DSC (TA 2920) was performed to provide data on the crystallization behavior used in the specimens sliced from the sample sheets. The specimens were crimp-sealed in 40-μL aluminum crucibles. All specimens were scanned from 20 to 180 at 10°C · min^{-1} to obtain the glass transition temperature and crystallinity of PLA without erasing their history.

Rheology.

Dynamic rheological properties of the PLA/PBAT/SPC blends were assessed using a

strain-controlled rheometer (DISCOVERY HR-2). Samples were tested using a parallel-plate geometry (*d*=25 mm) operated at 165 °C. All samples were cut from compounding sheets after conditioning. The sample was loaded between the parallel plates. Parallel plates subsequently compressed the sample to 1mm thick prior to each test. A strain sweep test was initially conducted to determine the linear viscoelastic region of the materials. A dynamic frequency sweep test was subsequently performed to determine the dynamic properties of the blends. The strain and frequency range used during testing were 1% and 500 to 0.05 rad/s, respectively. Steady-state shear tests at the same temperature were also conducted to investigate the viscosity-shear rate relationship.

Dynamic Mechanical Analysis (DMA).

Dynamic mechanical properties of PLA/PBAT/SPC composites and effect of plasticizer were studied by a Rheometrics Solids Analyzer (RSAII). DMA specimens ($1 \times 13 \times 35$ mm^3) were cut from extruded sheet samples and tested using a single-cantilever fixture at 1 Hz vibration frequency. All tests were conducted at a strain of 0.03% using a 2 $°C \cdot min^{-1}$ temperature ramp from -50 to 150 °C.

Water Absorption.

Sheet samples were in the form of a bar 76.2mm (3 in.) long by 25.4mm(1 in.) wide, as noted by ASTM D570-98. All samples were first dried at 50±3°C for 24 h and then kept in a desiccator until they reached room temperature. Accuracy of data for immediately weighed samples should be with in 0.001g. Subsequently, placing the dried samples in distilled water at 23±1°C for certain intervals, usually two-hour, over night, twenty-fore hour and also long-term. Next, the samples were removed from the water, and tissue paper was used to erase excess surface water.

Finally, the samples were weighed. Five applications were used from each formulation. The water absorption was calculated on a dry sample weight basis.

Results and Discussion

Tensile Properties.

Depending on its composition, interfacial adhesion and morphological structure, the mechanical properties of a polymer blend may vary (Hobbs et al. 1988; Dell'Erba et al. 2001). PLA and PBAT have complementary mechanical properties. While PLA is of high strength and modulus but brittle, PBAT is soft and highly ductile. Therefore, the blends of PLA an PBAT exhibit moderate strength and toughness and significant high ductility (Jiang et al. 2006). When SPC was introduced to this system, the morphological structure and interfacial properties became more complex. Because of the poor compatibility between the components in the ternary blends, low strength was noted for all the ternary blends. To improve the mechanical properties of the blends, effective compatibilization for the blends is desirable.

In Table3.2, compared with the control sample, the blends with PLA-g-MA exhibited significant higher strength and modulus but lower elongation. For the blend containing 3% PLA-g-MA, the strength and modulus were increased ~15% and 20% to that of the uncompatibilized one, respectively. However, a sharp decrease in elongation took place. Further increasing PLA-g-MA content from 3 to 6% did not result in significant changes in these properties. This result suggests that the 3% PLA-g-MA had probably saturated the interface. MA-grafted PLA has been found to serve as an effective compatibilizer for PLA/SPC composites (Zhu et al. 2012). Our previous studies showed that both the grafting degree and concentration of maleated PLA had a significant effect on the morphology and properties of

PLA/SPC composites. The tensile properties of the compatibilized PLA/SPC composites were significantly higher than that of the uncompatibilized one (Zhu et al. 2012).

The addition of 3% PEOX in the blends had little effect on the tensile strength of the blend, but increased elongation. The elongation of the blend containing 3% PEOX was twice that of the blend without PEOX. Further increasing PEOX from 3 to 6% led to a ~10% additional increase in elongation, and tensile strength and modulus of the blends remained essentially unchanged. PEOX and SPC were found to be miscible (Zhang et al. 2006; Liu et al. 2010). Therefore, PEOX appears to dissolve in the SPC phase, which led to the change of its surface tension and was more compatible with PLA and PBAT. Notably, the addition of PEOX as a compatibilizer in the PLA/SPC binary blends resulted in fine dispersion of SPC in the PLA matrix but had little effect on improving tensile strength (Zhang et al. 2006; Liu et al. 2010). Because PEOX does not contain the reactive groups which can form covalent bonds with PLA or PBAT, we speculate that the interfacial adhesion between PEOX-modified SPC and PLA was sufficient for it to form fine dispersion in the matrix but still not strong enough to impart high strength for the blends.

In this study, the elongation of the blends was found to increase from 21.6 to 40.0% with addition of 3% of PEOX. The elongation continued to increase with PEOX content, but at a much smaller pace. In binary blend systems, i.e. PLA/SPC and PBAT/SPC blends, PEOX helps to achieve fine dispersion of SPC in the matrix but has little effect on elongation(Zhang et al. 2006; Liu et al. 2010). As shown in Table 2.2, the ternary blend without the addition of PEOX and ATBC behaved in a brittle manner, with an elongation of only 2.6%. This indicates that the PEOX and ATBC likely had a synergetic effect to improve the ductility of the PLA/PBAT/SPC blends.

Our study found that using PLA-g-MA as a compatibilizer in PLA/PBAT binary blends

increased the tensile strength and modulus and decreased elongation. The morphological structure also became finer with the addition PLA-g-MA. These results indicate that PLA-g-MA could compatibilize the PLA/PBAT blends(Teamsinsungvon et al. 2012). Like PLA-g-MA, PBAT-g-MA cold similarly work as a compatibilizer in the PLA/PBAT blends. PLA-g-MA and PBAT-g-MA have demonstrated good compatibilizing effects on the PLA/SPC (Zhu et al. 2012) and PBAT/SPC blends (Chen and Zhang 2010), respectively. In this work, among the three interfacial modifiers, PBAT-g-MA demonstrated the least compatibilizing effect for the blends. With 3% PBAT-g-MA, the strength of the blend increased slightly, but elongation suffered a ~50% decrease. With 6% PBAT-g-MA, the strength decreased slightly and elongation was reeducated by ~40% with respect to the uncompatibilized blend.

When PEOX and PBAT-g-MA were used as compatibilizers, the modulus of the resulting blends decreased, particularly when the latter was used. However, PLA-g-MA-modified blends exhibited an increased modulus with respect to that of the control group. This change of modulus by type of interfacial modifier was generally consistent with the corresponding change in tensile strength. These results suggest that when PEOX and PBAT-g-MA are used as compatibilizers, the core-shell structure (in which SPC was included in PBAT) was dominant in the resulting blends. In contrast, when PLA-g-MA is used as a compatibilizer, SPC and PBAT are more likely to disperse separately in the PLA matrix.

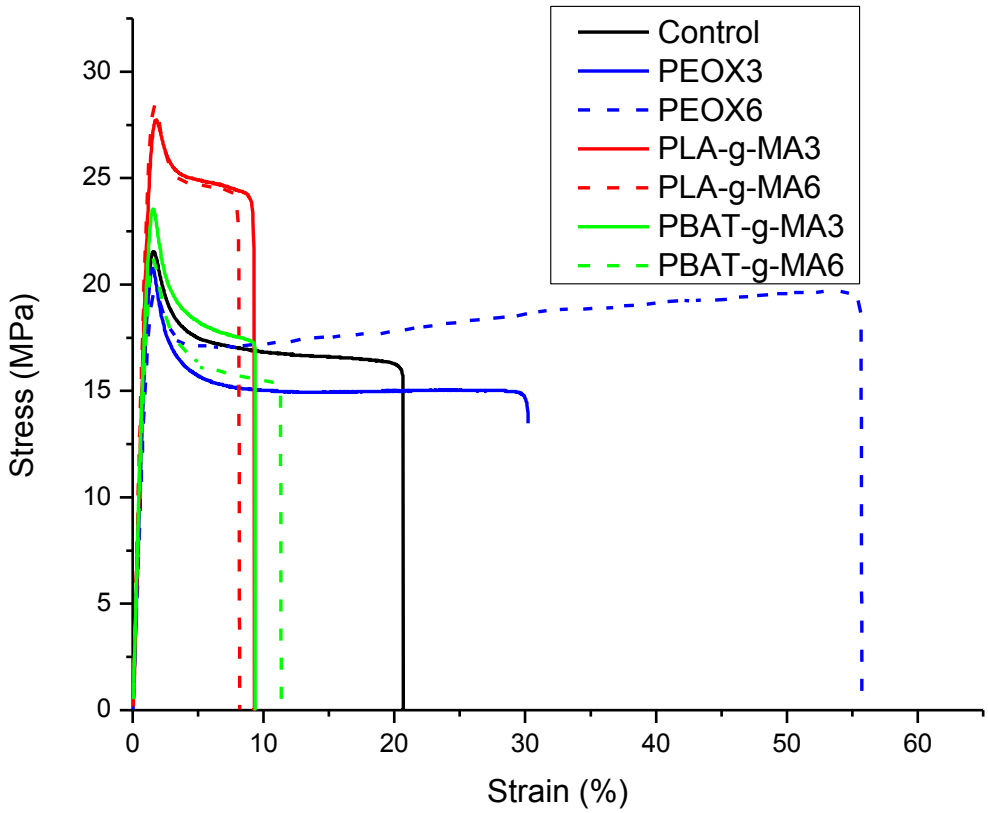
Table 3.2 tensile test results of PLA/PBAT/SPC blend with different compatibilizer.[1]

Sample name	Strength (MPa)	Strain (%)	Modulus (GPa)
Control	21.3 ± 0.2	21.6 ± 0.8	2.30 ± 0.05
PEOX3	23.6±1.1	40.0±3.5	2.08±0.16
PEOX6	22.2 ± 0.5	45.7 ± 8.6	2.06 ± 0.26
PLA-g-MA3	28.3 ± 0.8	9.2 ± 1.1	2.59 ± 0.04
PLA-g-MA6	28.6 ± 4.1	7.6 ± 1.2	2.42 ± 0.26
PBAT-g-MA3	22.9 ± 0.8	11.0 ± 3.4	2.08 ± 0.06
PBAT-g-MA6	20.7 ± 0.4	12.6 ± 2.3	1.87 ± 0.11

[1] The PLA/PBAT/SPC ratio in the blend was fixed at 50:20:30 (w/w/w) and all samples have 3% of ATBC.

In Figure 3.1, all stress versus strain curves show clear yield points (maximum load) and stable necking growth through cold drawing. The blends with PLA-g-MA show the highest stress and lowest elongation among the three curves. With increasing PLA-g-MA content, the stress increased and elongation decreased dramatically (Zhu et al. 2012). The strength of the blends rose ~30% with addition of 3% of PLA-g-MA. When PEOX or PBAT-g-MA was used as a compatibilizer, the stress was similar to that of the blend without compatibilizer. As it is shown later, the stable necking growth through cold drawing was found to be due to the debonding of the plasticized composite (Jiang et al. 2006).

Figure 3.1 Stress-strain curves of PLA/PBAT/SPC blends with different concentration of compatibilizers

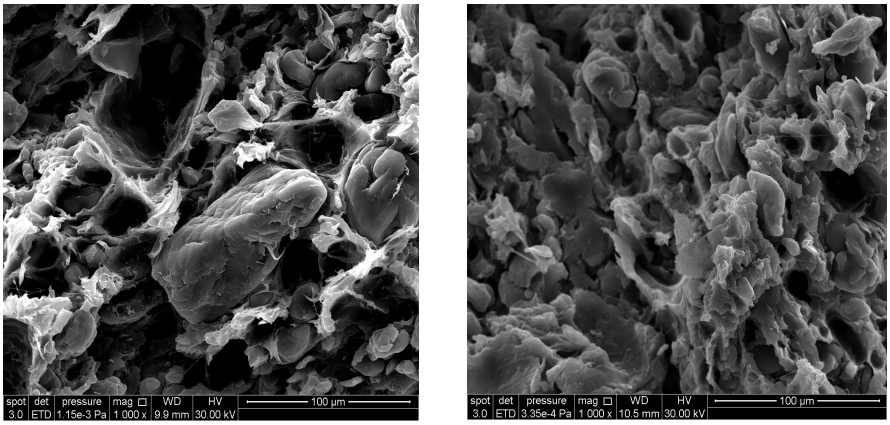


Morphology of tensile fractures

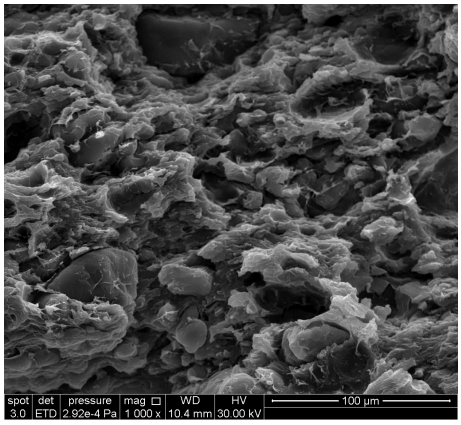
The mechanical properties of a polymer blend largely depend on its morphology, which in turn is determined by the interfacial adhesion, blend composition and viscosity ratio, and processing conditions (Willemse et al. 1999; Lee and Han 2000; Elias et al. 2007). In Figure 3.2, the tensile fracture surfaces differed significantly between the PLA/PBAT/SPC blends with and without compatibilizers (Willemse et al. 1999). The control sample without compatibilizer

exhibited a coarse surface and the dispersed particles appeared large and not well-wetted, indicating poor interfacial adhesions in the blends. This result was mainly due to the large difference between SPC with PLA and PBAT. While the former is highly hydrophilic, the latter two are hydrophobic. Previous studies also demonstrate that the binary blends of SPC with PLA or with PBAT without use of compatibilizer have very coarse phase structures. However, the addition of compatibilizer, whether PLA-g-MA or PBAT-g-MA, results in ternary blends exhibiting phase structures with particles that are much more finely dispersed with much better wetting. Among the three compatibilizers, PLA-g-MA led to the finest phase structure for the blends, indicating that it likely produced higher interfacial bonding than the other two in the blends. This finding accords with results for tensile properties which indicate that PLA-g-MA compatibilized blends exhibit the highest tensile strength and modulus.

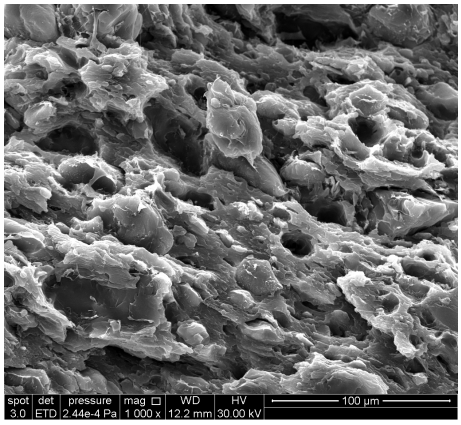
Figure 3.2 SEM micrographs of tensile fracture surfaces of PLA/PBAT/SPC (50/20/30 w/w/w) blends



Control PEOX6



PLA-g-MA6



PBAT-g-MA6

Thermal properties

In Figure 3.3, PLA displayed three transitions: the glass transition, cold crystallization and melting (Wang et al. 2001; Jiang et al. 2006; Zhang et al. 2006; Liu et al. 2010). Since PBAT is a minor component in the blends and its glass transition temperature (T_g) of around -20 °C is not very sensitive to DSC testing, the T_g of PBAT was determined from the DMA test. Although PLA is a semi-crystalline polymer, without further treatment such as the addition of nucleating agent or reduction in the cooling rate during the processing, it was difficult to obtain PLA products of high crystallinity (Jiang et al. 2006; Zhang et al. 2006; Chen et al. 2008). In Figure 3.3, the cold crystallization temperature decreased with the addition of PEOX. Crystallinity of PLA in the blends also increased slightly with addition of PEOX. These results indicate that PEOX may be useful as a nucleation agent as well, although it was not very efficient one. In contrast, the addition of PLA-g-MA and PBAT-g-MA in the blends had little effect on the T_g of PLA, but decreased crystallinity slightly.

Figure 3.3 DSC thermograms of PLA/PBAT/SPC composites comprising different concentration of PLA-g-MA

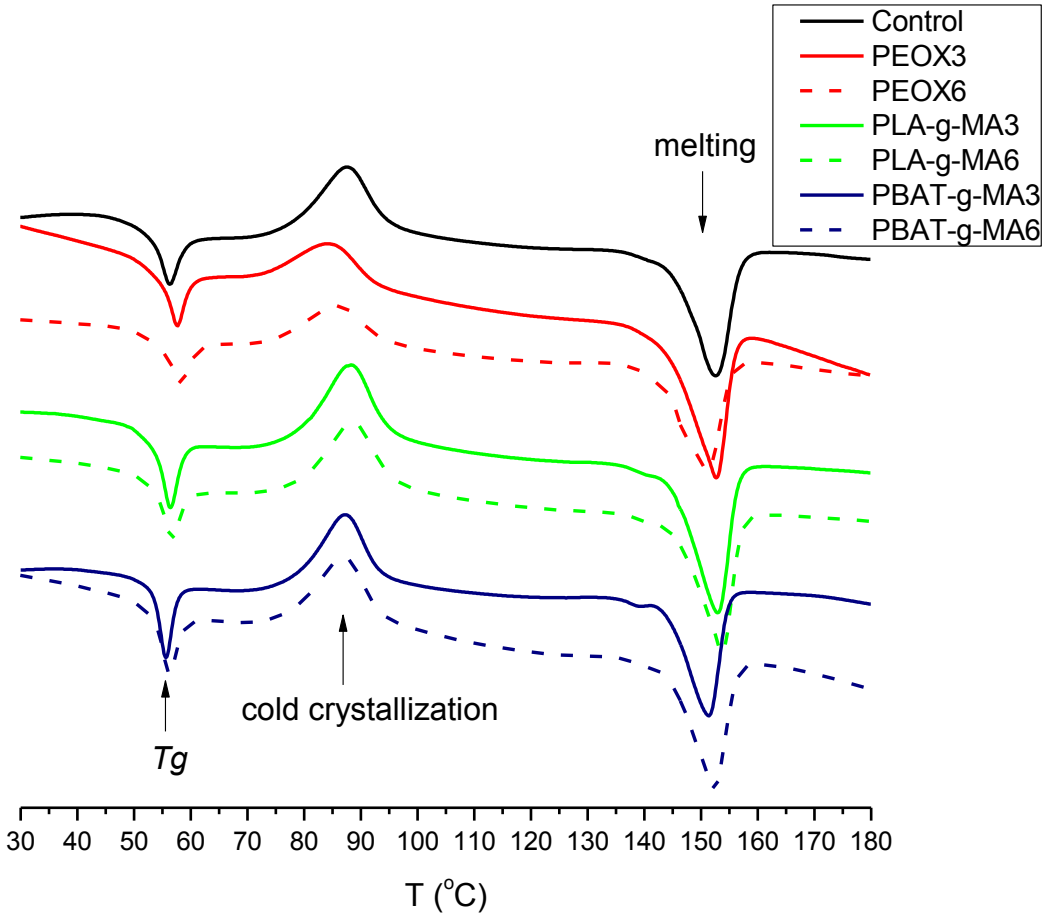


Table 3.3 DSC results of the PLA/PBAT/SPC composites with different compatibilizer.[1]

Sample	T_g (°C)	Cold crystallization		Melting		Crystallinity (%)[3]
		T_{cc} (°C)	ΔH_{cc} (J/g)[a]	T_m (°C)	ΔH_m (J/g)[2]	
Control	56.3	87.7	8.4	152.8	12.8	5.1
PEOX3	58.8	84.7	6.7	153.0	14.3	8.8
PEOX6	58.3	86.3	7.4	151.3	13.5	7.1
PLA-g-MA3	56.5	88.3	12.4	153.2	14.6	2.6
PLA-g-MA6	56.7	88.7	12.6	154.0	14.6	2.3
PBAT-g-MA3	55.7	87.3	12.1	151.5	12.3	0.2
PBAT-g-MA6	56.3	87.2	10.5	152.7	12.4	2.2

[1] All samples contain 3% of ATBC.

[2] Data corrected for the percentage of PLA in the blend. The heat of fusion of 100% crystalline PLA is 86J/g(Chen et al. 2009).

[3] Crystallinity= $\frac{H_m - H_{cc}}{H_{PLA}} \times 100\%$.

Rheological properties.

Dynamic rheology tests under the oscillatory shear are widely used to detect structural characteristics and properties for multi-component or multi-phase polymer systems, due to their sensitive response to structural changes in heterogeneous polymers. The state of dispersion of fillers also strongly affects rheological properties (Macosko and Larson 1994; Zhang et al. 2006; Liu et al. 2007). Before testing, a dynamic time sweep test was conducted to select the testing conditions. These tests occurred under 1% strain at 165 $°C$ from 500 to 0.05 rad/s.

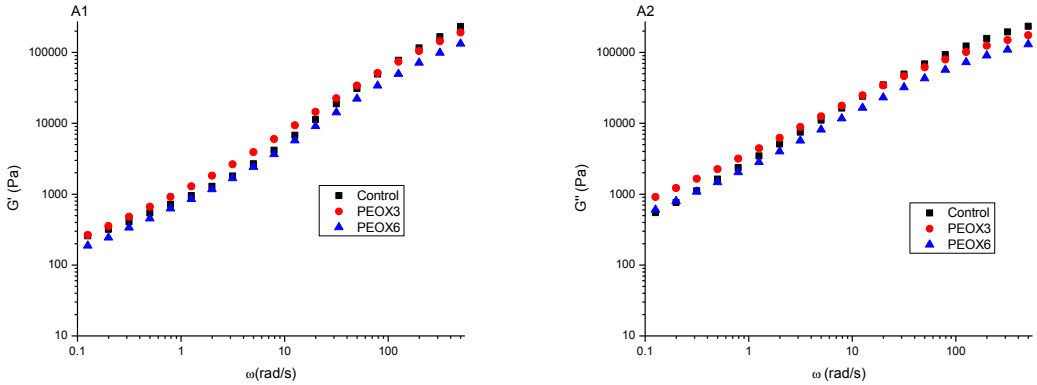
Figure 3.4 shows the storage modulus (G′), loss modulus (G″) and complex viscosity ($\eta*$) of the ternary polymer blends. With increasing frequency, all PLA/PBAT/SPC blends show a shear thinning behavior at high frequencies. The addition of PBAT-g-MA caused an increase in viscosity and storage modulus. However, the addition of PEOX and PLA-g-MA reduced the viscosity and storage modulus. Since the complex viscosity and storage modulus mainly depends on the viscosity and elasticity of the added components (Jiang et al. 2006), we can assume that the combination of interfacial adhesion (Liu et al. 2010) and the dispersion state (Huang et al. 2006) of fillers led to the final results.

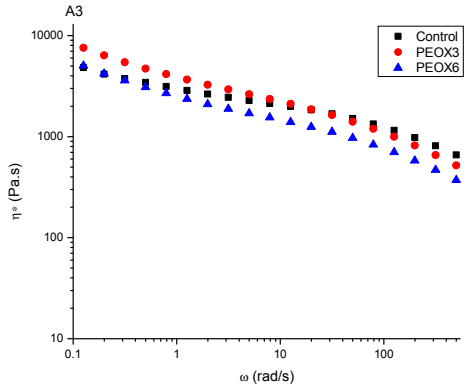
However, the slope of the G' decreased within the terminal zone in the composites with compatibilizer. From Table 3.4, as PEOX content increased, the slopes (n, scaling exponent) of (G') vs. (ω) changed from 0.67 to 0.79 when PEOX content changed from 0 to 6%. As PLA-g-MA changed from 0 to 6%, the slopes changed from 0.68 to 0.71. When PBAT content changed from 0 to 6%, the slopes changed from 0.68 to 0.54. This decreasing frequency-independence of G' suggests that the melt becomes liquid-like at low frequencies with additional PBAT-g-MA. The increase of the soft content of PBAT mainly causes this result. In addition, the increasing frequency-independence of G' indicates that the melt becomes solid-like at low frequency with additional PEOX or PLA-g-MA. This solid-like behavior of the blends indicates that the blend phase forms an interacted network structure with a long relaxation time.

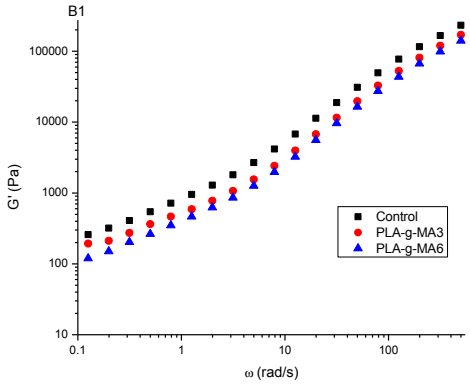
Table 3.4 Slopes in the terminal zone

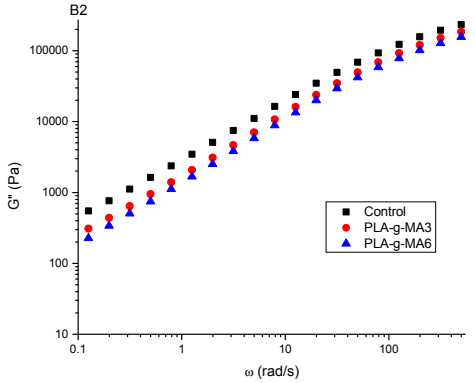
Sample No.	Slopes in the terminal zone	
	$\log(G')/\log(\omega)$	$\log(G'')/\log(\omega)$
Control	0.68	0.83
PEOX3	0.72	0.73
PEOX6	0.79	0.75
PLA-g-MA3	0.67	0.88
PLA-g-MA6	0.71	0.90
PBAT-g-MA3	0.59	0.61
PBAT-g-MA6	0.54	0.61

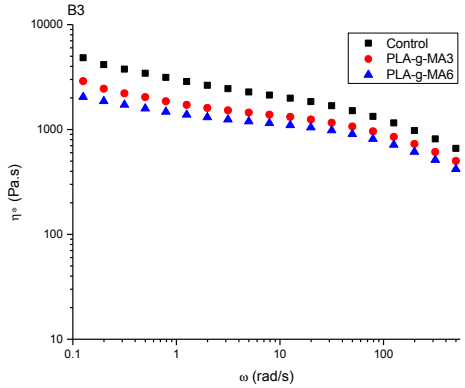
Figure 3.4 Dynamic frequency sweeps of PLA/PBAT/SPC blends. Strain=1% and T=165℃.

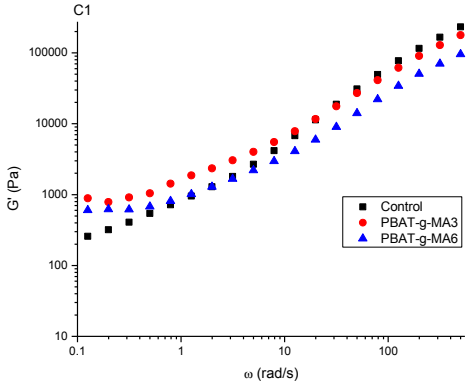


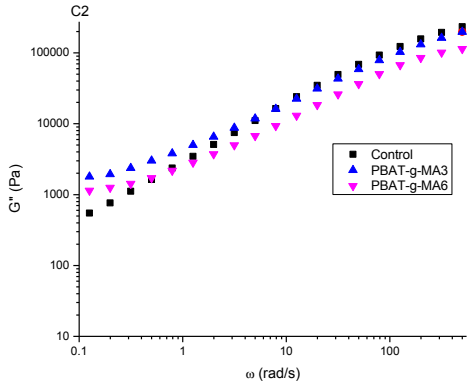

A3
Control
PEOX3
PEOX6
η* (Pa.s)
ω (rad/s)

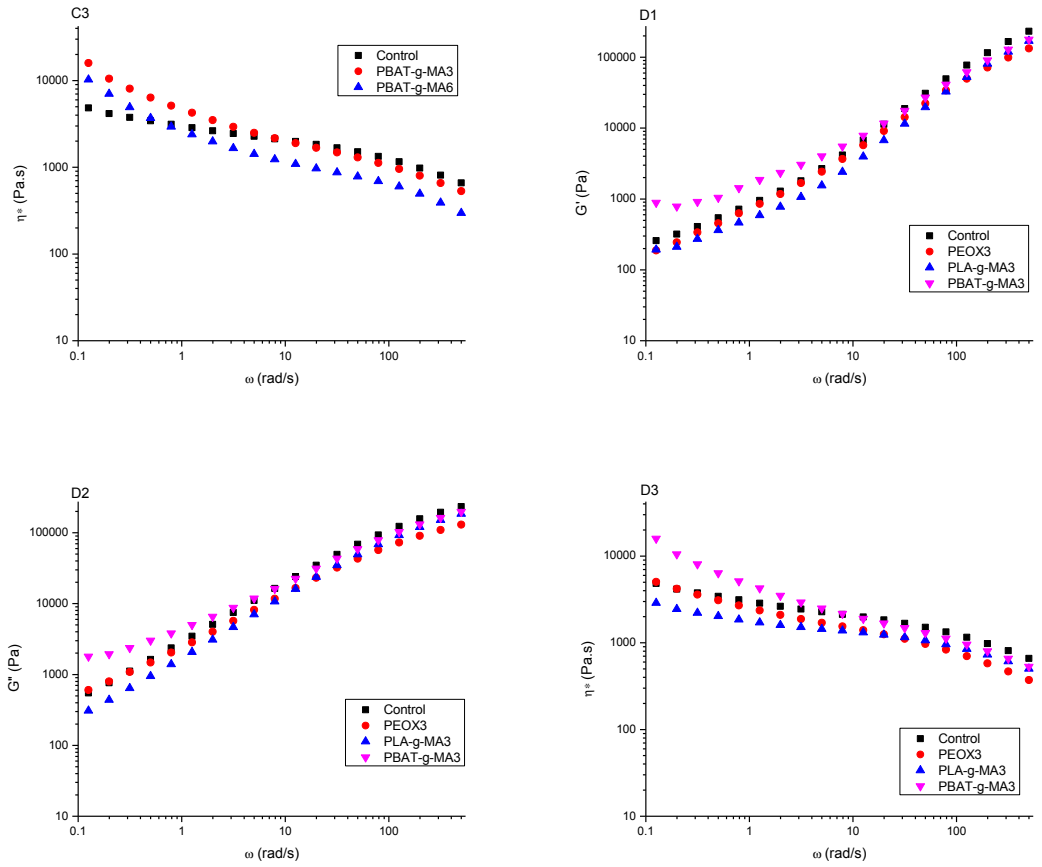

B1
Control
PLA-g-MA3
PLA-g-MA6
G' (Pa)
ω (rad/s)


B2
Control
PLA-g-MA3
PLA-g-MA6
G'' (Pa)
ω (rad/s)


B3
Control
PLA-g-MA3
PLA-g-MA6
η* (Pa.s)
ω (rad/s)


C1
Control
PBAT-g-MA3
PBAT-g-MA6
G' (Pa)
ω (rad/s)


C2
Control
PBAT-g-MA3
PBAT-g-MA6
G'' (Pa)
ω (rad/s)



A1, A2, A3: Blends with 3% of ATBC using PEOX as compatibilizer

B1, B2, B3: Blends with 3% of ATBC using PLA-g-MA as compatibilizer

C1, C2, C3: Blends with 3% of ATBC using PBAT-g-MA as compatibilizer

D1, D2, D3: Blends with 3% of ATBC using 3% different compatibilizers

Dynamic mechanical properties

As noted in the last chapter, the dynamic mechanical properties of the blends are also greatly affected by phase structure. Compared with DSC, DMA is more sensitive to transitions and can detect transition temperatures, which could not be revealed in DSC testing. In Figure 3.5, three main transitions are noted for all PLA/PBAT/SPC blends. The glass transition of PBAT was

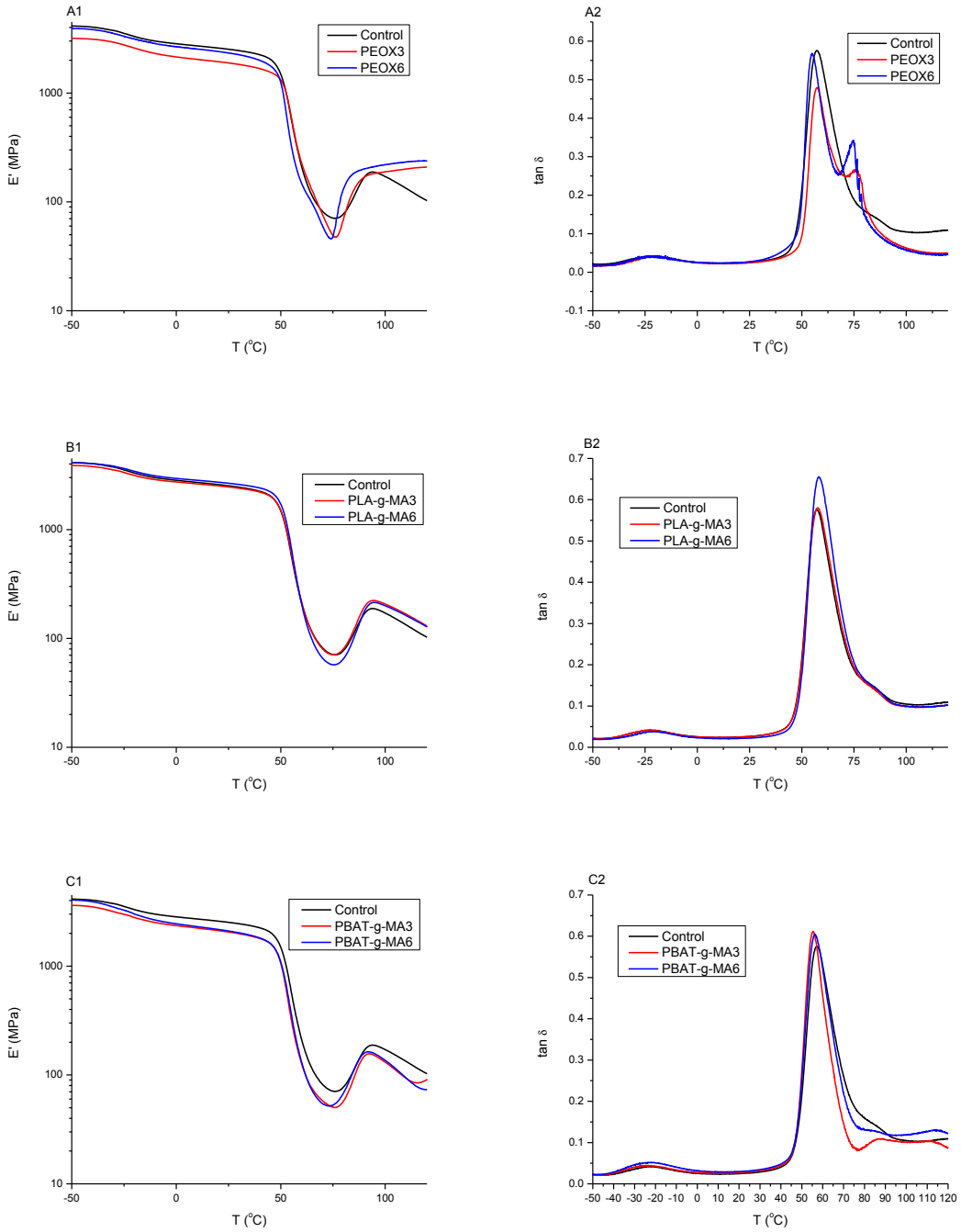
around -25 $°C$. The transition of about 60 $°C$ was attributed to the T_g of PLA. The cold crystallization of PLA around 90 $°C$ is also shown in the figures. In the blends with PEOX, another damping peak at about 75 $°C$ appeared. This transition was attributed to the glass transition of the SPC phase. The T_g of neat SPC is about 160 $°C$ and T_g of PEOX was about 70 $°C$. Since PLA and PEOX were miscible and most of the residual moisture was in the SPC domain, the T_g of the SPC domain in this blend was greatly suppressed. In Table 3.5, using PLA-g-MA and PBAT-g-MA to compatibilize the blends, the T_g of PLA and PBAT shifted towards each other. This indicates enhanced interaction between the PLA and PBAT phases, induced by PLA-g-MA and PBAT-g-MA. These interactions induced by compatibilizers in accord with tensile, rheology properties, and morphology characterization of the blends discussed previously.

Table 2.5 storage moduli in different temperature and glass transition temperature of PLA/PBAT/SPC blends

Sample No.	E' (MPa)			T_g (°C)		
	25 °C	60 °C	120 °C	1	2	3
Control	2423	211	103	-24.3	55.8	/
PEOX3	2489	262	177	-21.6	56.1	72.1
PEOX6	2336	147	238	-25.6	56.4	72.8
PLA-g-MA3	2522	216	130	-27.9	56.3	/
PLA-g-MA6	2724	208	127	-25.8	57.0	/
PBAT-g-MA3	2121	126	91	-30.1	54.5	/
PBAT-g-MA6	2172	126	73	-26.1	55.5	/

Figure 3.5 Effect of compati

bilizer on dynamic mechanical properties of PLA/PBAT/SPC (50/20/30) blends.



A1, A2: Blends with 3% of ATBC using PEOX as compatibilizer

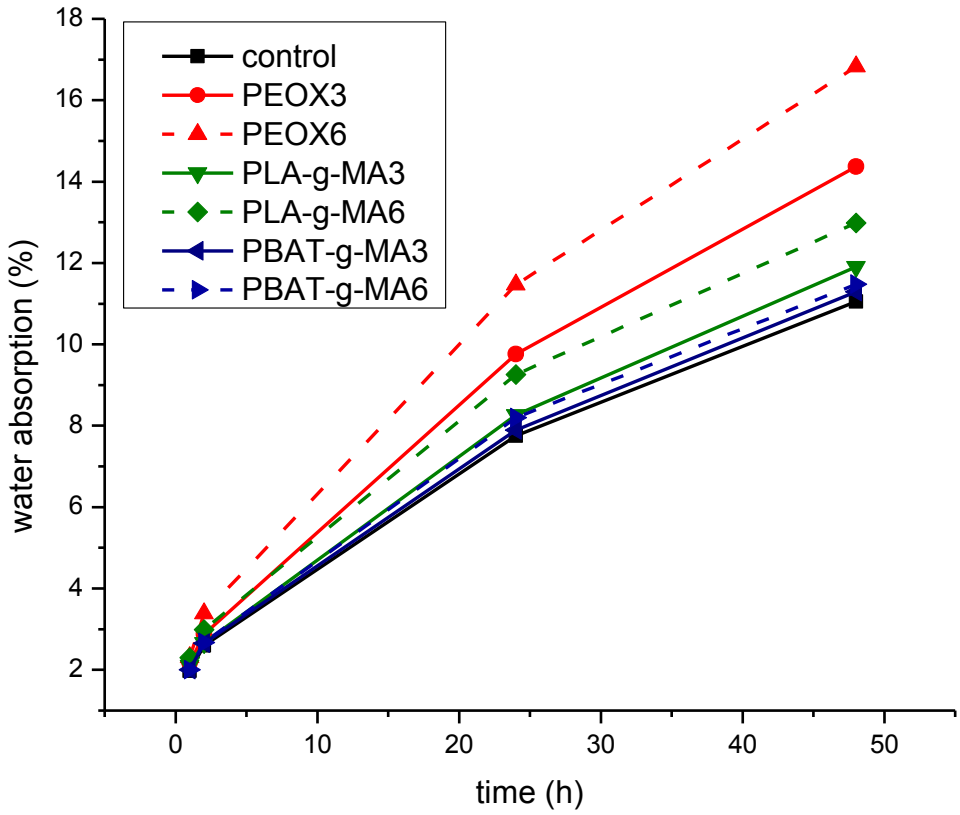
B1, B2: Blends with 3% of ATBC using PLA-g-MA as compatibilizer

C1, C2: Blends with 3% of ATBC using PBAT-g-MA as compatibilizer

Water absorption

The hydrophobic PLA absorbed little water in immersion tests, showing a water uptake of only ~0.8% (Liu et al. 2010) at equilibrium. Since SPC is highly hydrophilic due to the polar functional groups such as amino and hydroxyl groups, the PLA/PBAT/SPC blends exhibited a much higher water uptake than pure PLA or PBAT. In Figure 3.6, all the three compatibilizers increase the water absorption. That is mainly because compatibilizer makes the SPC domains become finer and the threads more elongated (Chen and Zhang 2010) in a percolation structure. This network structure causes the soy proteins to connect to each other, so water easily flows through the soy protein network from the outside into the inner parts. Since PEOX is water-soluble polymer, while PLA-g-MA and PBAT-g-MA are insoluble, the sample with PEOX has the highest water absorption among all the three compatibilizers.

Figure 3.6 water absorption of PLA/PBAT/SPC blends with different compatibilizer.



Conclusions

In soy-based ternary blends, PEOX, PLA-g-MA and PBAT-g-MA were shown to be effective for improving the properties of PLA/PBAT/SPC. The tensile properties of the compatibilized PLA/PBAT/SPC composites are all improved at low concentrations. Among the three compatibilizers, PLA-g-MA showed the highest tensile strength and modulus. PEOX showed great improvement in elongation with similar strength and modulus, compared with uncompatibilized blends. The addition of compatibilizers resulted in fine phase structure of the

composites and SPC domains. Dynamic rheology properties indicate that the phase of blends formed an interacted network structure. Dynamic mechanical properties of the composites, which were greatly affected by the phase structure indicates better interfacial adhesion when compatibilizers were present. Finally, the increasing water absorption created a percolation structure with addition of compatibilizers.

Chapter 4 Conclusions

This study examined the mechanical and physical properties of the ternary polymer blends are investigated in order to contribute to the knowledge base on better materials for bio-based plastics used in food container, beverage cup or some other one-off applications. Since SPC is hydrophilic and PLA, PBAT are hydrophobic, the interfacial adhesions among them are weak. Therefore, addition modifiers should be taken into this ternary blends. This study examined two kinds of additives for modifying the properties of soy-based composites to improve performance. Chapter 2 described the effect of ATBC as a plasticizer on the properties of the composites. Chapter 3 discussed different kinds of compatibilizers, including PEOX, PLA-g-MA and PBAT-g-MA, as well as their effect on the properties and phase structure of the ternary blend.

Results show that sufficient water is needed in the pre-compounding of SPC to increase elongation. With 10 wt% on the base of SPC, mechanical properties improved much more than with 5 wt% of water. With increasing ATBC, the toughness of the compound improved significantly. This was found to be an even more effective plasticizer in the PLA/PBAT/SPC blend than other PLA blend previously studied. Improved dispersion and phase morphology were also noted.

Chapter 3 described efforts to compatibilize the blends of PLA/PBAT/SPC using PEOX, obtained PLA-g-MA and PBAT-g-MA. PLA-g-MA increased tensile strength and modulus most effectively among the three compatibilizers. The other two compatibilizers also created some improvement in tensile strength. It is notable that the strain at the break increased more than 100%, even with 3% of PEOX, while other compatibilizers showed hardly any increase in strain. Small ratios of PBAT-g-MA were shown to increase strength, but with 6% of PBAT-g-MA, the

strength was reduced due to the properties of PBAT-g-MA itself. However, the phase morphologies all improved when compatibilizers were used; good interfacial bonding and dispersion was also shown in the results.

This work indicates that this biodegradable polymer blends is very effective for making one-off applications with good mechanical properties and competitive price. However, further research is needed on the dispersion state and phase morphology of these materials.

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