

**THE ROLE OF ZINC IONOMER IN THE IMPACT PERFORMANCE OF
POLYLACTIDE (PLA) TERNARY BLENDS: EFFECT OF ACID
CONTENT AND DEGREE OF NEUTRALIZATION**

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A thesis submitted in partial fulfillment of
the requirements for the degree of

Master of Science in Materials Science and Engineering

WASHINGTON STATE UNIVERSITY
School of Mechanical and Materials Engineering

May 2011

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ACKNOWLEDGEMENT

I would like to thank my advisor and mentor Dr. Jinwen Zhang, for his generous help and instruction through all phases of my research. His dedication to research greatly inspires me to further my own efforts. I also want to thank my two other committee members Dr. Katie Zhong and Dr. David Field, for their valuable advice and support on my thesis research. I want to express my special thanks to Dr. Hongzhi Liu for his immense help on the guidance of lab instruments and valuable suggestions in addressing the problems in my research. My appreciation is also extended to the staffs of the Composite Materials and Engineering Center: Bob Duncan, Brent Olson and Scott Lewis for their help resolving technical and administrative problems and also Patricia Smith, Suzanne Hamada and Janet Duncan for their generous help and patience. I also want to thank all fellow graduate students in CMEC for their support and help. I also want to thank Ms. Mary Simonsen, our graduate academic coordinator, for her generous help throughout the time I pursued this degree. Finally I want to give the deepest appreciation to my parents and friends for their support.

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Abstract

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May 2011

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In this work, polylactide (PLA) was blended with an epoxy-containing elastomer (ethylene/n-butyl acrylate/glycidyl methacrylate, 'EBA-GMA'), and a zinc ionomer (partially neutralized ethylene/methacrylic acid copolymer, 'EMAA-Zn'). Un-neutralized ethylene/methacrylic acid copolymers (EMAA-H) were used in the place of EMAA-Zn ionomers as controls. In order to study the effect of acid content and degree of neutralization of zinc ionomer on the impact behaviors of the PLA/EBA-GMA/EMAA-Zn (or EMAA-H) ternary blends, EMAA-Zn with various degree of neutralization were derived from two types of EMAA-H containing 15 wt% and 4 wt% methacrylic acid (MAA) comonomer, respectively. Degree of neutralization of EMAA-Zn was determined by Fourier transform-infrared (FT-IR) spectroscopy. The concentration of zinc oxide incorporated into the ionomers was characterized by thermogravimetric analysis (TGA). The mechanical properties of the blends were studied by notched Izod impact tests and tensile tests and the fracture surfaces were investigated by scanning electron microscopy (SEM). Two important reactions involved in the processing of the

PLA/EBA-GMA/EMAA-Zn (or EMAA-H) ternary blends, i.e. the interfacial compatibilization between EBA-GMA and the PLA matrix and the crosslinking reaction of EBA-GMA, were studied. Interfacial compatibilization reaction between the epoxy functionalities of EBA-GMA and the terminal hydroxyl groups of PLA was studied using FT-IR. Crosslinking reaction of EBA-GMA in the presence of EMAA-Zn (or EMAA-H) was investigated by torque rheology and its crosslinking level was studied using dynamic mechanical analysis (DMA). The particle size and substructure of the dispersed domains were analyzed using images acquired from transmission electron microscopy (TEM). It was found that neutralization was necessary for the blend to have superior impact strength. The impact strength of blends containing EMAA-Zn with high initial content of MAA were universally higher than that of blends containing EMAA-Zn with low initial content of MAA, regardless of the neutralization degree. The results of this study implied that a good interfacial adhesion between dispersed particles and the PLA matrix, a proper crosslinking level of the EBA-GMA phase and a fine particle size were favorable for high impact toughness of these PLA/EBA-GMA/EMAA-Zn ternary blends.

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Abbreviation

PLA	Poly lactide or poly(lactic acid)
EBA-GMA	Ethylene/n-butyl acrylate/glycidyl methacrylate
MAA	Methacrylic acid
EMAA-H	Ethylene/methacrylic acid
EMAA-Zn	Partially neutralized ethylene/methacrylic acid ionomer
PLA/EBA-GMA/EMAA-Zn	A ternary blend containing polylactide, ethylene/n-butyl acrylate/glycidyl methacrylate and partially neutralized ethylene/methacrylic acid ionomer
PLA/EBA-GMA/EMAA-H	A ternary blend containing polylactide, ethylene/n-butyl acrylate/glycidyl methacrylate and un-neutralized ethylene/methacrylic acid copolymer
FT-IR	Fourier transform-infrared spectroscopy
TGA	Thermogravimetric analysis
DMA	Dynamic Mechanical Analysis
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy

Chapter 1 Introduction

1.1 Advantages, synthesis and applications of polylactide (PLA)

Poly(lactide or poly(lactic acid) (PLA) is a biodegradable aliphatic polyester produced from renewable resources. It is a sustainable alternative to petroleum-based polymers. Lactic acid from which PLA is produced can be obtained from the bacterial fermentation of agricultural products such as corn starch or other carbohydrate-rich substances like maize, sugar and wheat. PLA can be synthesized either by polycondensation of lactic acid or ring opening polymerization of lactide (the dimer of lactic acid). Polycondensation may not directly yield PLA of sufficiently high molecular weight and chain extension reactions are probably needed (Zhong et al 1999). In the later synthesis route, two steps are involved. Lactic acid is first converted into lactide ring intermediates and then a metal salt catalyst is employed in the ring-opening polymerization process to produce the polylactide polymer (Ovitt and Coates 1999; Cheng et al 1999). From this method a wide range of molecular weights can be obtained.

PLA as a bioplastic can be used to produce disposable food containers, cups for cold beverage, packaging bags etc. In the form of fabrics, PLA finds its applications in agriculture and horticulture as protective clothing or in medical and health care as operating gown, surgical mask etc. It has also been evaluated as a material for tissue engineering (Roether et al 2002). PLA is more expensive than many petroleum-derived commodity plastics, but its price has been falling as its production increases. PLA has as good mechanical properties in terms of strength and modulus as many other conventional petroleum-based polymers have and hence it can potentially be used in place of them. However, PLA has a major weakness, i.e. its inherent brittleness, which limited its applications.

1.2 State-of-the-art polylactide (PLA) toughening

In recent years, PLA toughening has been extensively investigated. It was demonstrated that by varying the stereochemistry, molecular weight and crystallinity of PLA, its toughness can be improved to some extent, however, the influences of which is usually only marginal (Anderson et al 2008). Main strategies that have been employed in toughening PLA are plasticization (Ljungberg and Wesslén 2002; Murariu et al 2008), copolymerization (Grijpma et al 1991; Jing and Hillmyer 2008) and melt blending with a variety of flexible polymers or rubbers. Among these, melt blending is the most practical and economic way to toughen PLA. PLA has been blended with various biodegradable or non-biodegradable polymer modifiers, including poly(butylene adipate-co-terephthalate) (PBAT) (Jiang et al 2006; Zhang et al 2009), polycaprolactone (PCL) (Semba et al 2006; López-Rodríguez et al 2006), poly(ether) urethane elastomer (PU) (Li and Shimizu 2007), polyhydroxyalkanoate copolymers (PHA) (Schreck and Hillmyer 2007), poly (butylene succinate) (PBS) (Harada et al 2007; Wang et al 2009), polymerized soybean oil (Robertson et al 2010), acrylonitrile-butadiene-styrene copolymer (ABS) (Li and Shimizu 2009), poly(ethylene octene) (PEO) (Su et al 2009), thermoplastic polyolefin elastomer (Ho et al 2008). In most of above mentioned PLA blends, although the tensile toughness (ductility) of PLA blends is greatly increased with respect to that of neat PLA, its impact toughness (impact strength) showed very limited improvement.

Reactive blending is a strategy that has been employed in many flexible-polymer toughened polymer blend systems, in most of which, the main purpose is to compatibilize the two or more immiscible blend components. In such a reactive blending, chemical reactions take place at the interface, and copolymers form in situ to serve as compatibilizers which greatly improved the interfacial and in turn mechanical properties of the blends. A few PLA blends prepared by

reactive blending achieved ‘super toughness’ (Anderson et al 2003; Anderson and Hillmyer 2004; Oyama 2009), which was defined as possessing a notched impact strength higher than 530 J/m (Wu 1990). PLA/poly(ethylene-glycidyl methacrylate) (EGMA) (80/20, w/w) blends prepared by Oyama through reactive blending had an impact strength up to 50 times of that of neat PLA after annealing the injection-molded samples at 90 °C for 2.5 hrs (Oyama 2009). The author found that the crystallization of PLA played an important role in achieving the high impact toughness. However the contribution of interfacial adhesion and morphological evolution with the annealing were not discussed in that study. Another super toughened PLA/PE blends were prepared by Anderson et al. using PLA-*b*-PE diblock copolymers as compatibilizers (Anderson et al 2003; Anderson and Hillmyer 2004). The copolymer structure on the interfaces of matrix and dispersed phase was found correlated to the mechanical properties of the blends. However, a more comprehensive understanding of the toughening mechanism of super toughened PLA blends is still needed.

Recently, a novel super toughened PLA ternary blend system comprising an epoxy-functionalized rubber (ethylene/n-butyl acrylate/glycidyl methacrylate terpolymer, ‘EBA-GMA’) and a zinc ionomer (partially neutralized ethylene/methacrylic acid copolymer, ‘EMAA-Zn’) was introduced by our group (Liu et al 2010; Liu et al 2011). The melt blending process involves simultaneous reactive compatibilization between the dispersed phase and the PLA matrix and dynamic vulcanization (crosslinking) of the epoxy-containing rubber (EBA-GMA). This PLA blends demonstrated super toughness and moderate tensile strength and modulus. Studies on the effect of blending temperature showed that it had a great influence on the impact strength of these blends and the best results were obtained at 240 °C (Liu et al 2010). The effect of blend composition was also studied previously. Under a fixed total modifier

loading of 20 wt. % (i.e. PLA/EBA-GMA/EMAA-Zn 80/20-x/x), the impact strength increased rapidly with a small amount of ionomer (i.g. at EBA-GMA/EMAA-Zn ratio of 19/1, w/w) and continued to rise to a maximum value at EBA-GMA/EMAA-Zn ratio of 15/5 (w/w) at 240 °C (Liu et al 2010). When the EBA-GMA/EMAA-Zn ratio continued to decrease and became less than 1, the impact strength suffered from a rapid deterioration due to poor interfacial adhesion resulted from phase-inversion of EBA-GMA phase and EMAA-Zn phase (Liu et al 2011). When phase-inversion happened, the substructure (phase structure inside of particles) of dispersed phase changed from that the ionomer was encapsulated in the rubber phase to that the rubber was encapsulated in the ionomer phase. From these studies, it was shown that high blending temperature (240°C) greatly accelerated both the compatibilization and crosslinking reactions, and zinc ion catalyzed both of the reactions (Liu et al 2010). Investigation of micromechanical deformation suggested that low cavitation resistance of rubber and suitable interfacial adhesion between rubber phase and PLA matrix were responsible for the optimal impact toughness achieved (Liu et al 2011).

1.3 Flexible-polymer toughening via melt blending

Rubber-modified polymers have been developed and commercialized since as early as 1940s, such as HIPS. There are several important factors controlling the toughening effect obtained through this strategy. A better understanding of these factors as well as mechanisms of rubber toughening is necessary to guide us through choosing suitable parameters to achieve the optimal toughening effect in a specific system.

1.3.1. Effect of particle size

There are different types of polymer matrices in terms of their intrinsic brittleness. The intrinsic brittleness of polymers is determined by two chain parameters, namely, the

entanglement density, v_e , and the characteristic ratio, C_∞ (Wu 1990). Type I matrix refers to the brittle polymer which fails primarily by crazing. Type II matrices are also called pseudoductile matrices, which have high unnotched impact strength but are very notch-sensitive, and they fail mainly by shear yielding. Toughening mechanism of a polymer blend depends on the intrinsic brittleness of the matrix (Wu 1990).

For matrices primarily fail by crazing, on the one hand, it was observed that the ease of craze initiation is related to the size of the particle, and that crazes are rarely nucleated from particles with a size smaller than 1 μm (Donald and Kramer 1982). Small rubber particles are incapable in initiating crazes due to their lack of efficiency in influence the stress field far enough into the surrounding matrix. On the other hand, the modifier particles also need to be sufficiently large to stop the crazes (Wu 1990). In addition, cavitation was found easier to occur in larger particles (Bucknall et al 1994). It has been observed that an optimum particle size exists for effective rubber toughening of brittle matrices such as PS, PMMA, SAN, and epoxy resins (Okamoto et al 1991; Hobbs 1986; Cigna et al 1989; Wrotecki et al 1991). The optimum particle size has been found decreasing when the matrix becomes more ductile in rubber-toughened PS (Okamoto et al 1991; Hobbs 1986), SAN (Cigna et al 1989), and PMMA (Wrotecki et al 1991) blends. In pseudo-ductile (type II) matrices, a sharp brittle-ductile transition was observed as the particle sizes of the toughening agents become smaller (Wu 1988). Instead of optimum particle size, a critical ligament thickness (CLT) model (the percolation theory) was proposed in nylon blend systems (Wu 1988; Wu 1990). The effective toughening size of rubber particles can be very small because the cavitation is not necessary for such matrices (Wu 1990). Gloaguen et al. (Memon and Muller 1998) have shown that in rubber-toughened PMMA the transition from difficult to easy for the shear band formation, as the rubber volume fraction varied, occurred at a

unique critical interparticle (shell to shell) matrix ligament thickness.

PLA is an intrinsically brittle matrix with a characteristic ratio, C_{∞} , of ca. 9.5~11.8 (Grijpma et al 1994; Joziassse et al 1996; Cooper-white et al 1999) depending on the L/D lactide ratio. Therefore the existence of an optimum particle size for toughened PLA system is possible (Wu 1990). In fact, it was reported recently the range of optimum particle diameter of 0.5~0.9 μm for toughening PLA, by correlating tensile toughness with dispersed particle diameter in PLLA/conjugated soybean oil binary blends (Robertson et al 2010). Optimum particle size was also reported in systems involving matrix with PLA-like properties (Cho et al 1998; Cho et al 1997; Huang et al 2006; Oshinski et al 1996; Takaki et al 1997). However, due to the complexity of toughening mechanism, there is so far no solid conclusion with respect to the existence of the optimum particle size in PLA blend systems.

1.3.2 Cavitation resistance and the crosslinking degree of rubber phase

Toughening of a polymer requires large amount of energy be absorbed or dissipated before the material fails. In rubber-toughened blend systems, the energy dissipation process is initiated by the rubber particles, which dispersed in the matrix as a separate phase and act as stress concentrators. Microvoiding initiated by stress concentration occurs either inside of the rubber particles (cavitation) or at the interface between the particle and the matrix (debonding). Because of the microvoiding, the hydrostatic tension in the material is released and the stress field inside the thin ligaments of matrix between the voids is converted from triaxial stress into plane stress (Lazzeri and Bucknall 1993). The Predominant mechanism in blends of many polymers such as polyamide (PA) (Borggreve et al 1989), polycarbonate (PC) (Parker et al 1990), and epoxy resins (Yee and Pearson 1986; Becu et al 1997) of the improved toughness was found to be cavitation of the rubber particles followed by extensive shear yielding throughout the matrix. The

energy-balance model developed by Bucknall et al. predicts that cavitation happens more easily when the particle size is increased and when the modulus is reduced (Bucknall et al 1994). The higher degree of crosslinking can result in higher rubber modulus which affects the efficiency of the rubber particles as stress concentrators and at the same time tends to enlarge the particle size. It was suggested that the rubber modulus must be less than or equal to that of the matrix to be suitable as a stress concentrator in polyamide blends (Du Pont patent, Epstein 1977). On the other hand, a certain level of crosslinking the rubber was believed desirable because it allows the rubber to reach high strains by fibrillation, and the fibrils would have high strength (Bucknall et al 1979). Therefore, a suitable crosslinking degree is probably favorable for the best toughening effect.

1.3.3 Interfacial compatibilization

The interfacial property between the rubber modifiers and the matrix is important in obtaining fine particles, good dispersion and good stress transfer between the matrix and the modifier particles. A polymer blend comprising two immiscible components is usually desirable for toughening. However, poor interfacial adhesion leads to poor mechanical properties of the blend (Paul 1978). Therefore, such blends need to be compatibilized properly. One of the common strategies of interfacial compatibilization is known as physical compatibilization or non-reactive compatibilization which involves a premade copolymer as an interfacial agent with its segments chemically identical to or miscible with the blend components (Cho et al 1996; Chun and Han 1999; Ruckdäschel et al 2007). The compatibilizer is synthesized separately before added to the blend during melt-mixing. The disadvantages of this method are that it is relatively complex and expensive to synthesis the copolymers and they may not always locate at the interface of the blend components.

Another strategy is known as reactive compatibilization conducted by melt blending of polymers with suitable functionalities or by adding small functional molecules. It is achieved by in situ formed graft copolymers locating at the interface of dispersed particles and matrix acting as compatibilizers. Unlike in the non-reactive or physical compatibilization, a precursor of the compatibilizer instead of a compatibilizer itself is added into the blend. Reactive blending is often employed in polymer blends consisting of a non-reactive plastic such as polyolefin or polystyrene (PS) and a reactive one such as polyester or polyamide (PA) (Lee and Char 1994; Seo et al 2007). The functionalities of the precursors commonly come from monomers such as acrylic acid (AA) (Filippi et al 2002), or maleic anhydride (MAH) (Xu et al 2008), or glycidyl methacrylate (GMA) (Hale et al 1999), which react with terminal groups such as hydroxyl and carboxyl of polyesters or amino groups of polyamides to form compatibilizers in situ. In some cases, the precursors of compatibilizers react with both of the blend components chemically. In situ compatibilization of blends containing polyester by using epoxy-containing polymers was shown to be effective since the carboxyl and hydroxyl terminal group of polyesters can both react with the epoxy functionalities (Mika et al 1973). The ethylene-co-glycidyl methacrylate (EGMA) copolymer is found to be an efficient reactive compatibilizer for polymer blends of poly(butylene terephthalate) (PBT) and polypropylene (PP) (Tsai and Chang 1996).

1.3.4 Substructure of impact modifier particles

Impact modifier with core-shell structures have been employed in toughening of thermoplastics such as polystyrene (PS) (Guo et al 2003), polypropylene (PP) (Ou et al 1999), and thermosets such as epoxy networks (Becu et al 1997). Multi-phase impact modifiers offer an interesting possibility for obtaining optimum toughening effects if the morphologies are properly controlled and the interfacial interactions is adequately achieved (Gui et al 2010; Xu et al 2010).

The micromechanical processes and toughening mechanisms can be influenced by morphology and substructure of modifier particles.

A very well known example of use of core-shell impact modifiers is high impact polystyrene (HIPS) which contains rubber particles with a large number of small polystyrene (PS) subinclusions as the optimal morphology for PS toughening (Fischer and Hellmann 1996). In the particles with so called “salami” (i.e. multi-core) structure occluded polystyrene accommodates the displacements due to crazing by local fibrillation of the rubber surrounding each occlusion, without the formation of large voids. Therefore, this “salami” structure of rubber particles is critical for the toughening effect (Fischer and Hellmann 1996). Core-shell particles based on natural rubber (NR) containing hard PS subinclusions within the soft rubbery core showed a more efficient toughening effect on PS than those without PS subinclusions (Schneider et al 1997). This effect was attributed to the enhanced rubber fibrillation during deformation because of the introduction of the PS subinclusions, which prevented a particle matrix separation and permitted a larger extent of plastic deformation before failure, as evidenced by scanning electron microscopy (SEM) observations (Schneider et al 1997).

Many core-shell impact modifiers are pre-made core-shell particles consist of a crosslinked rubbery core, typically butadiene-based, and a hard glassy shell, typically of poly(methyl methacrylate) (PMMA), which is grafted on to the rubber and they are generally made via emulsion polymerization (Wu et al 2004; Wang and Li 2000). For premade core-shell impact modifiers, the hard shells not only provide fast stress transfer but also prevent the rubbery core from fusing together during melt processing. The shell is sometimes modified with reactive monomers such as maleic anhydride (MA), acrylic acid (AA), or glycidyl methacrylate (GMA) to achieve compatibilization between the shell and the matrix (Hale et al 1999; Sun et al 2008;

Ajji and Chapleau 2002). Functionalized core-shell impact modifiers such as styrene-maleic anhydride (SMA) copolymers (Lu et al 1996) and glycidyl methacrylate (GMA) functionalized methyl methacrylate-butadiene-styrene (MBS) were blended with polyamide-6 (Aerdt et al 1997). For core-shell or multi-phase impact modifiers formed during melt blending, the particle size, substructure, and physical properties are not pre-determined but rather largely depend on the extent of reactions occur during processing.

1.3.5 Ionomers

An ionomer is an ion-containing polymer with (usually 10~15 mol %) ionic groups along the backbone chains or as pendant groups. Ionomers were used alone or with other polymers to modify the toughness of various polymer matrices such as polystyrene (PS) (Bellinger et al 1994), polyethylene terephthalate (PET) (Ohishi 2004), polyamide (PA) (Leewajanakul et al 2003), and polyoxymethylene (POM) (Wang and Cui 2005). Ionomers were also used as compatibilizer in polymer blends (Xie et al 2006; Xu et al 1999; Leewajanakul et al 2003; Montoya et al 2010) or polymer composites (Cui et al 2009; Su et al 2006; Li and Yan 2007). Most commonly used ionomers are partially neutralized ethylene acrylic acid or methacrylic acid copolymers containing zinc or sodium cations, e.g. the carboxylate ionomer synthesized by DuPont via neutralization of the random copolymers, poly(ethylene-co-methacrylic acid) (EMAA) with zinc salt or its oxide. The neutralization of ionomers can be achieved either in solution (Kiekmeier et al 2002) or melt processing (Yano et al 1992). The extent of neutralization can be determined using infrared spectroscopy (Coleman et al 1990; Macknight et al 1968). Ionomers with a variety of properties can be obtained by altering the type of polymer backbone and cation, the carboxyl functionality content, and the degree of neutralization.

1.4 Research objectives

Melt blending is the most economic and practical way to toughen PLA. While the tensile toughness (ductility) of PLA blends in the literature is greatly increased with respect to that of the neat PLA, its impact toughness (impact strength), which is critical for many engineering applications, showed very limited improvement in most of the cases. Although a few supertoughened PLA blends (>530 J/m of notched impact strength (Wu 1990)) were reported (Anderson et al 2003; Anderson and Hillmyer 2004; Oyama 2009), the mechanism of such super-toughening effect still need to be better understood. In our recently introduced PLA/EBA-GMA/EMAA-Zn ternary blends, the impact properties of the blends depended on the two reactions involved during mixing, namely, the interfacial compatibilization between the dispersed phases and the PLA matrix and the crosslinking of EBA-GMA. During melt blending, the epoxy groups of the elastomer can react with both the hydroxyl end groups of the PLA matrix and carboxylic acid groups of the ionomer, i.e. the partially neutralized EMAA-Zn ionomer. Zinc ion of the ionomer acted as catalyst for both reactions. The former reaction results in the formation of in situ graft copolymer of PLA onto elastomer backbones, which serves as the compatibilizer between the elastomer and PLA matrix phases. The latter reaction results in the crosslinking of the elastomer. The extent of either reaction depends on the presence of catalysts as well as the concentration of carboxyl groups in the EMAA ionomers. The morphological structure, physical properties of modifier particles and the interfacial adhesion are governed by the above mentioned two reactions and they all together have an effect on the impact toughness of the blends. Therefore, there is a critical need for understanding the role of zinc ionomer in the impact performance of PLA ternary blends by studying the effect of acid content and the degree of neutralization. In the previous results, the Izod notched impact strength

of the ternary PLA/EBA-GMA/EMAA-Zn (80/20-x/x, w/w) blends was investigated as a function of weight ratio of EBA-GMA/EMAA-Zn. Based on the previous study (Liu et al 2010), the optimum ratio of EBA-GMA/EMAA-Zn at which the maximum impact strength (ca. 860 J/m) was achieved, was found to be 15/5 by weight. Thus, this weight ratio of EBA-GMA/EMAA-Zn was chosen to be used in this work. Ternary blends of PLA/EBA-GMA/EMAA-Zn (80/15/5, w/w/w) were prepared through reactive blending at fixed composition, temperature (240 °C) and other conditions. The effect of acid content and the degree of neutralization on impact toughness of PLA/EBA-GMA/EMAA-Zn ternary blends were studied.

The long-term goal of the research is to develop economically viable and eco-friendly PLA alternatives to petroleum-based polymer materials. Specifically, the overall objective of this study is to achieve high-impact PLA ternary blends by using zinc ionomer with optimized characteristics and obtains the optimal interfacial property, crosslinking degree of rubber and blend morphologies which are responsible for high impact performance. The central hypothesis of this research is that superior impact toughness of the PLA ternary blends requires a suitable balance between the reactive interfacial compatibilization and the crosslinking reaction of EBA-GMA, which largely depends on the degree of neutralization (i.e., the zinc ion/carboxyl acid group ratio) as well as the total contents of functionalities in the ionomer (determined by the initial methacrylic acid content in EMAA-H). This hypothesis is based on the studies on toughening mechanisms of polymer blends in the literature and the current finding of this novel PLA ternary blend. In order to test the central hypothesis and accomplish the objective of this research, the following two specific aims were pursued:

Specific Aim 1 Investigate the effect of acid content and the degree of neutralization of zinc ionomers on the impact performance of PLA ternary blends

The hypothesis for this aim is that under a given blend composition and blending conditions, the overall content of the functionalities and the ratio between two functionalities (i.e. the carboxyl group and the zinc ionic group) determined by the degree of neutralization are probably two other important factors which result in different extent of crosslinking reaction of EBA-GMA and the reactive compatibilization. The *rationale* for the this aim is that based on the observation and understanding on how the overall acid content and degree of neutralization affect the two important reactions involved in the processing of this PLA ternary blends and in turn the final impact properties, optimal impact properties may be achieved by properly choosing the type of ionomers or precursors as well as the degree of neutralization of it.

Specific Aim 2 Study the effects of the interfacial compatibilization, crosslinking degree of rubber, the blend morphology and substructure of modifier particles on the impact behavior to further understand the role of zinc ionomers in the impact performance of PLA/EBA-GMA/EMAA-Zn ternary blends

The hypothesis for this aim is that suitable interfacial adhesion, crosslinking degree of rubber phase; particle size is responsible for the optimal impact toughness. The *rationale* for this specific aim is that with the knowledge of how the impact performance is influenced by the crosslinking degree of rubber, the interfacial compatibilization, the resulted morphology of the blends, and the substructure of modifier particles, it is possible to obtain better impact performance in this PLA/EBA-GMA/EMAA-Zn blend systems and probably also other polymer blend systems similar to this PLA ternary blend.

The research of my thesis is *creative and original*: the role of zinc ionomer in super tough PLA ternary blend systems has not been reported elsewhere. The expected outcomes of my research are: (1) Understanding of the influences of acid content and the degree of neutralization

of zinc ionomers on the two important reactions, i.e. interfacial compatibilization between EBA-GMA and PLA and the crosslinking reaction of EBA-GMA, involved in the reactive blending process and in turn on the impact performance of the PLA ternary blends; (2) Insights in the relationship between interfacial adhesion, crosslinking degree, phase structure, blend morphology and impact performance of PLA ternary blends.

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Chapter 2 Effects of total functionality and degree of neutralization of zinc ionomer on toughening of PLA/EBA-GMA/EMAA-Zn ternary blends

ABSTRACT

In this work, poly(lactic acid) (PLA) was blended with an epoxy-containing elastomer (ethylene/n-butyl acrylate/glycidyl methacrylate, 'EBA-GMA'), and a zinc ionomer (partially neutralized ethylene/methacrylic acid copolymer, 'EMAA-Zn'). EMAA-Zn with various degree of neutralization was prepared. Two kinds of EMAA-H with different initial content of methacrylic acid (MAA), high (15 wt. %) and low (4 wt. %), respectively, were used to prepare the zinc ionomers. Degree of neutralization of EMAA-Zn was determined using Fourier transform-infrared (FT-IR) spectroscopy. The total zinc oxide content in ionomers was characterized using thermogravimetric analysis (TGA). It was found that neutralization was necessary for the blend to have superior impact strength. The degree of neutralization of zinc ionomer has great influence on the impact strength while has little effects on the tensile properties of the blends. The impact strength of blends containing EMAA-Zn with high initial content of MAA were universally higher than that of blends containing EMAA-Zn with low initial content of MAA. The mechanical properties of PLA ternary blends were studied. The fracture surfaces from impact and tensile tests were studied using scanning electron microscopy (SEM).

Keywords: *PLA toughening, zinc ionomer, acid content, degree of neutralization, impact strength*

2.1 Introduction

Poly(lactic acid) is a commercially available renewable polymer which can be made into consumer items such as disposable plates and cups, packaging and clothing. However, the inherent brittleness of PLA prevents it from wide applications. Main strategies have been employed in toughening PLA include plasticization (Ljungberg and Wesslén 2002; Murariu et al 2008), copolymerization (Grijpma et al 1991; Jing and Hillmyer 2008) and melt blending with a variety of flexible polymers or rubbers. Among those strategies, melt blending is the most practical and economic way to toughen PLA. PLA has been blended with various biodegradable or non-biodegradable polymer modifiers, including poly(butylene adipate-co-terephthalate) (PBAT) (Jiang et al 2006; Zhang et al 2009), polycaprolactone (PCL) (Semba et al 2006; López-Rodríguez et al 2006), poly(ether) urethane elastomer (PU) (Li and Shimizu 2007), poly(hydroxyalkanoate) copolymers (PHA) (Schreck and Hillmyer 2007), poly(butylene succinate) (PBS) (Harada et al 2007; Wang et al 2009), polymerized soybean oil (Robertson et al 2010), acrylonitrile-butadiene-styrene copolymer (ABS) (Li and Shimizu 2009), poly(ethylene octene) (PEO) (Su et al 2009), thermoplastic polyolefin elastomer (Ho et al 2008). In most of above mentioned PLA blends, although the tensile toughness (ductility) of PLA blends is greatly increased with respect to that of the neat PLA, its impact toughness (impact strength) showed very limited improvement.

It has been shown that reactive blending was particularly effective in improving the impact performance of PLA blends (Anderson et al 2003; Anderson and Hillmyer 2004; Oyama 2009). These PLA blends achieved super toughness (>530 J/m of notched impact strength (Wu 1990)). PLA/ poly(ethylene-glycidyl methacrylate) (EGMA) (80/20, w/w) blends via reactive blending were prepared by Oyama. and the impact strength was found greatly improved up to 50 times of

that of neat PLA after annealing the injection-molded samples at 90 °C for 2.5 h (Oyama 2009). The author found that the crystallization of PLA played an important role in achieving the high impact toughness. However, the influence of interfacial properties and morphological parameters were not discussed in that study. Another super tough PLA/PE blends were prepared by Anderson et al. using PLA-*b*-PE diblock copolymers as compatibilizers (Anderson et al 2003; Anderson and Hillmyer 2004). The copolymer structure on the interfaces of matrix and dispersed phases were found correlated to the mechanical properties of the blends. However, the use of synthesized PLA copolymer is a less cost effective part in that approach. Furthermore, a more comprehensive understanding of the toughening mechanism of super toughened PLA blends is still needed.

In our recently reported work, PLA was reactively blended with an ethylene/n-butyl acrylate/glycidyl methacrylate terpolymer elastomer (EBA-GMA) and a zinc ionomer of ethylene/methacrylic acid copolymer (EMAA-Zn) (Liu et al 2010). These PLA blends demonstrated super toughness and moderate tensile strength and modulus. Effective interfacial compatibilization at elevated blending temperatures was found to be responsible for the significant increase in notched impact strength (Liu et al 2010). The blend which yielded the highest impact toughness was found to have a blend composition of PLA/EBA-GMA/EMAA-Zn ratio of 80/15/5 (w/w/w) and to be prepared at a blending temperature of 240 °C (Liu et al 2010).

In the preparation of the PLA/EBA-GMA/EMAA-Zn blends, two reactions, namely, the vulcanization (or crosslinking) reaction of EBA-GMA triggered by carboxylic acid groups of EMAA-H or EMAA-Zn and the reactive interfacial compatibilization between PLA and EBA-GMA, occurred simultaneously during melt-blending. Epoxy groups reacted with carboxyl groups to form ester linkages. The resulting hydroxyl groups from this reaction further reacted

with another epoxy group which led to the formation of crosslinked structure, i.e. the curing reaction. These reactions were dependent on the availability of carboxyl group, catalyst, and blending conditions. Our previous study showed that zinc ions catalyzed both curing of rubber and interfacial compatibilization reaction and carboxyl acid groups participated in both reactions (Liu et al 2010). Therefore, the acid content and degree of neutralization of the ionomers are anticipated to play important roles in controlling the extents of the above mentioned two reactions and therefore in determining the magnitude of impact strength of the blends. The two reactions involved in the processing of the PLA/EBA-GMA/EMAA-Zn ternary blends, as shown in Figure 2.1.

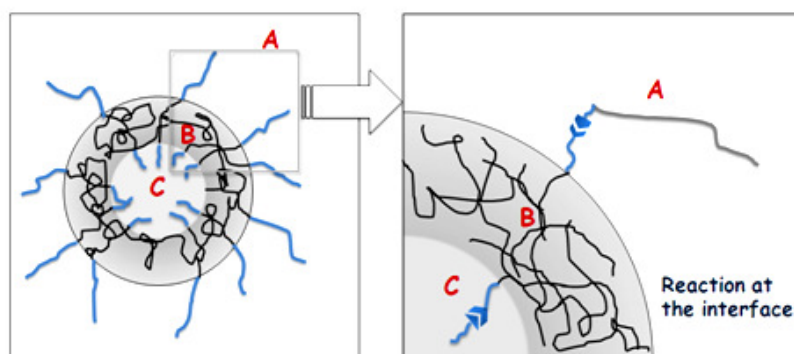
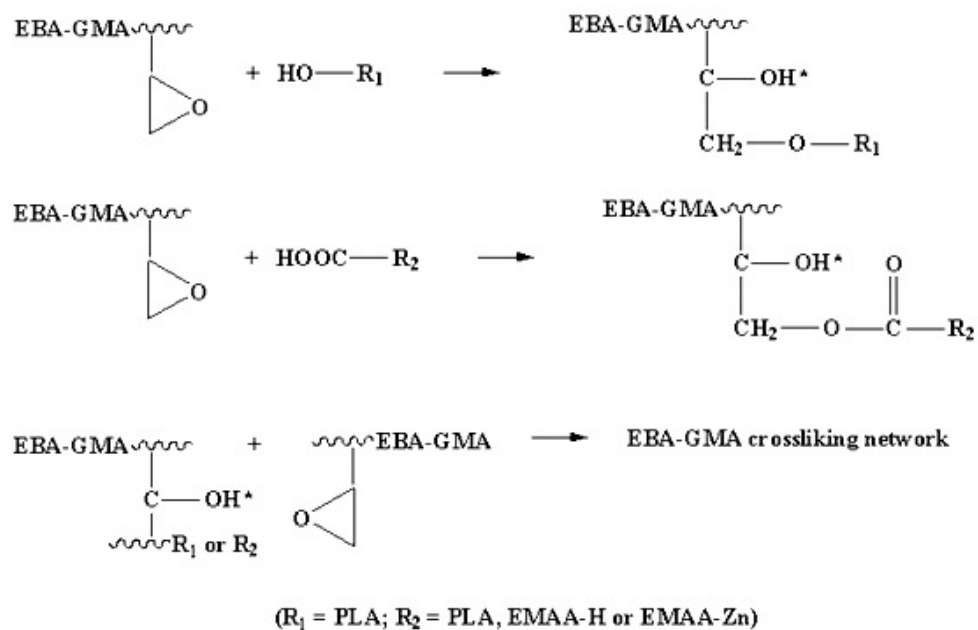


Figure 2.1 Reactions during reactive blending process at 240°C. PLA molecules were grafted at interfaces and crosslinking occurred inside EBA-GMA domains. (A: PLA; B: EBA-GMA; C: EMAA-H or EMAA-Zn).

2.2 Experimental

Materials. The materials used in this study and some specifications are listed in Table 3.1.

Table 2.1. Characteristics of materials used in this study

Material (abbreviation)	Grade (supplier)	Specifications
Poly(lactic acid) (<i>PLA</i>)	PLA2002D (NatureWorks)	MI (210°C, 2.16kg) = 5~7 g/10min
Ethylene/n-butyl acrylate/glycidyl methacrylate copolymer (<i>EBA-GMA</i>)	Elvaloy® PTW (DuPont Co.)	MI (190°C, 2.16kg) = 12 g/10min; melting point (DSC) = 72°C; E/BA/GMA = 66.75/28/5.25 (wt%) ¹
Ethylene/methacrylic acid copolymer (<i>EMAA15-H</i>)	Nucrel® 925 (DuPont Co.)	MI (190°C, 2.16kg) = 25 g/10min; melting point (DSC) = 92°C; methacrylic acid content = 15.0 wt%
Ethylene/methacrylic acid copolymer (<i>EMAA4-H</i>)	Nucrel® 0411HS (DuPont Co.)	MI (190°C, 2.16kg) = 11 g/10min; melting point (DSC) = 109°C; methacrylic acid content = 4.0 wt%
Zinc Oxide Powder (<i>ZnO</i>)	BAKER ANALYZED® Reagent (J.T. Baker Chemical Co.)	specific gravity 5.67 g/cm ³ ; melting point = 1975°C

¹ Kaci et al 2006

The EMAA-H copolymers containing 15 wt% and 4 wt% MAA were designated as EMAA15-H and EMAA4-H, respectively. The zinc ionomers derived thereof were designated as EMAA15-ZnX and EMAA4-ZnX, respectively, in which X referred to the percentage of neutralization. For example, ‘EMAA15-Zn60’ referred to the EMAA-Zn ionomer which had 60% of the carboxyl groups of its precursor (EMAA15-H) neutralized by ZnO.

Preparations of zinc ionomers. Prior to extrusions, EMAA-H pellets were oven-dried for at least 1 day at 80 °C and zinc oxide was oven-dried for at least 1 day at 150 °C. EMAA-H pellets were manually mixed with ZnO powders prior to extrusions. Neutralization reaction for

preparing zinc ionomers, i.e. EMAA-Zn, was conducted in a co-rotating twin screw extruder (Leistritz ZSE-18) with a screw diameter of 17.8 mm and an L/D ratio of 40 at a screw speed of 50 rpm. The temperature profile of the extruder barrels was 180/190/190/200/200/200/190/180°C from the first heating zone (next to feeding throat) to die, respectively. Vacuum at the 7th zone of the extruder was applied to eliminate small molecules generated during neutralization. The extrudates were pelletized and then extruded for a second time under the same condition in order to make the neutralization reaction more thorough and uniform. Likewise, the EMAA-H pellets without an addition of ZnO was processed also under the same conditions and was used as a control.

PLA ternary blend preparation. Prior to extrusions, the PLA pellets were dried for at least 1 day at 80 °C; EMAA-H or EMAA-Zn pellets obtained in the former step were dried for at least 1 day at 75 °C; EBA-GMA pellets were dried for at least 1 day at 65 °C. For all PLA ternary blends, the PLA content was fixed at 80 wt%, while the content of EBA-GMA and EMAA-Zn (or its un-neutralized precursor, EMAA-H) was fixed at 15 wt% and 5 wt% based on the total blend weight, respectively. Melt blending was performed using the same extruder at a screw speed of 50 rpm to prepare PLA/EBA-GMA/EMAA-Zn (80/15/5, w/w/w) and PLA/EBA-GMA/EMAA-H (80/15/5, w/w/w) ternary blends. The temperature of reactive extrusion was set at 240 °C. The barrels temperature profile of the extruder was set as 210/220/230/240/240/240/230/220°C from the first heating zone (next to feeding throat) to die, respectively. Prior to injection molding, the compounds were dried at 80 °C overnight in a convection oven. Specimens for mechanical properties measurement were injection molded (Sumitomo SE50D) at melt temperature of 190 °C and mold temperature of 35 °C. After injection molding, all test specimens were conditioned at 23 °C and 50% RH for 7 days prior to

testing and characterization.

Fourier transform-infrared spectroscopy (FT-IR). The spectra were recorded using a Thermo Nicolet Nexus 670 spectrometer (Nicolet). Thin films of EMAA-H and EMAA-Zn samples for FT-IR test were prepared by hot pressing at the same temperature as they were extruded, i.e. 200 °C. The thicknesses were measured using a screw micrometer with an accuracy of 1 µm.

Thermogravimetric analysis (TGA). TGA was performed on a Rheometric Scientific STA Thermogravimetric Analyzer. Each sample was scanned from 35 to 600 °C under a N₂ atmosphere at a heating rate of 10 °C min⁻¹.

Mechanical test. Notched Izod impact tests were performed according to ASTM D256 using a BPI-0-1 Basic Pendulum Impact tester (Dynisco, MA). Average value of five replicated specimens was taken for each composition. Tensile tests were conducted on a universal testing machine (Instron 4466) following ASTM D638. The crosshead speed was set at 2 in/min (50 mm/min) for all the samples and 0.2 in/min (5 mm/min) for some other samples. The initial strain was measured using a 2 in. extensometer.

Scanning electron microscopy (SEM). Impact fracture surfaces from Izod test and tensile fracture surfaces of the specimens were sputter coated with gold and then examined for morphological structure through a Quanta 200F field emission scanning electron microscope (FE-SEM, FEI Company) at an accelerated voltage of 15 kV.

2.3 Results and Discussion

2.3.1 Degree of Neutralization of EMAA-Zn determined by FT-IR

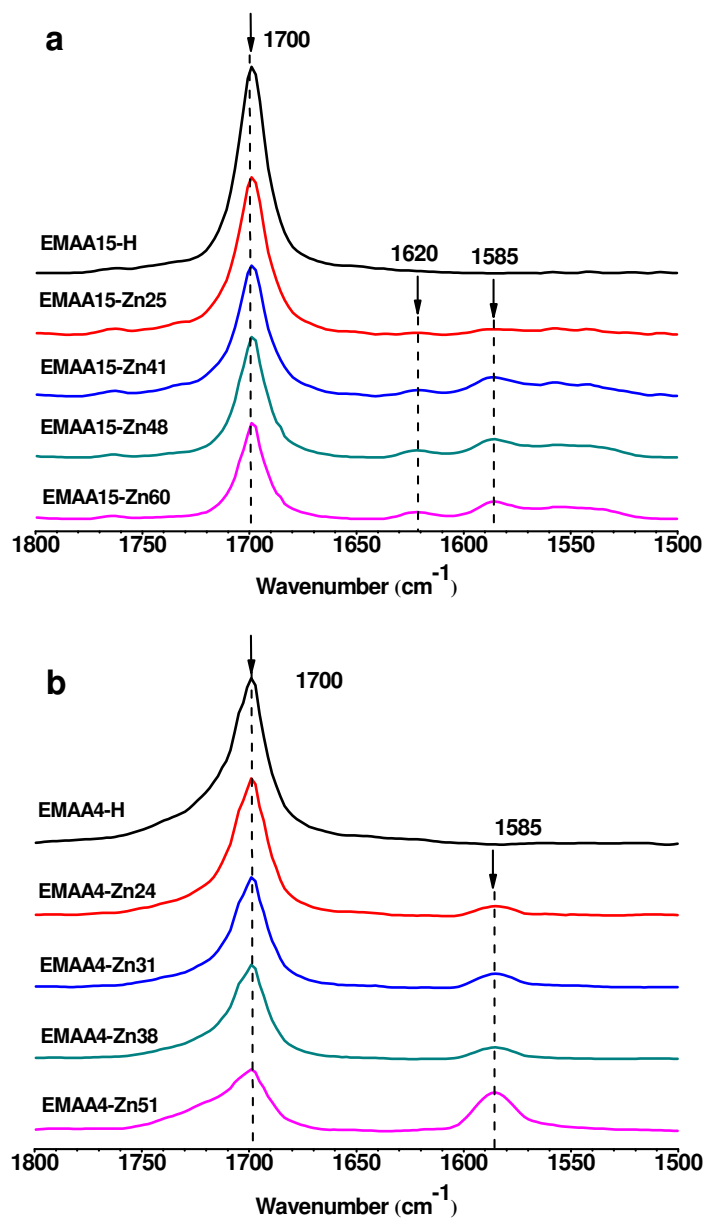


Figure 2.2 FT-IR absorption spectra of ionomer precursors and ionomers in the range of 1500~1800 cm^{-1} . a: EMAA15-H (A) and EMAA15-Zn with degrees of neutralization of 25% (B); 41% (C); 48% (D) and 60% (E); b: EMAA4-H (A) and EMAA4-Zn with degrees of neutralization of 24% (B); 31% (C); 38% (D) and 51%(E).

Prior to neutralization in extrusion process, ZnO and EMAA-H in various predetermined stoichiometric ratios were mixed in a plastic bag. However, because ZnO was in a fine powder form, it was unavoidable that ZnO was partially lost by sticking on bag, hopper and feed throat. Therefore, the actual ZnO incorporated after compounding would be lower. TGA was used to determine the actual incorporated amounts of ZnO, which was designated as the theoretical degree of neutralization under the assumption of complete reaction of ZnO with carboxylic acid groups during extrusion process. Nevertheless, polymer reactions in melt state are greatly limited by restricted diffusion and steric hindrance, and can rarely proceed to high completion in a short residence time. Therefore, the actual degree of neutralization was expected to be lower and needed to be determined via other methods. FT-IR was used in this study to determine the actual degree of neutralization of EMAA-Zn based on the precursor copolymers with 15 wt % and 4 wt % of methacrylic acid (MAA), respectively. The unreacted carboxyl groups existed primarily in the form of carboxyl acid dimers with a stretching frequency appears at 1700 cm^{-1} (Coleman et al 1990). The degree of neutralization were determined based on the integrated absorbance of the 1700 cm^{-1} carboxyl stretching band per unit sample thickness as shown in the following equation (Macknight et al 1968).

$$\text{Degree of neutralization} = \left[1 - \frac{\text{Area}_{1700\text{cm}^{-1}}/\text{thickness}(\text{EMAA} - \text{Zn})}{\text{Area}_{1700\text{cm}^{-1}}/\text{thickness}(\text{EMAA} - \text{H})} \right] \times 100\%$$

Figure 2.2 (a, b) shows the absorption spectra of EMAA-Zn samples in the range of $1500\sim 1800\text{ cm}^{-1}$. As shown in Figure 2.2, for EMAA-H, besides the absorption attributed to carboxylic acid dimers at 1700 cm^{-1} , there were no other significant absorptions in the region of $1500\sim 1700\text{ cm}^{-1}$ attributed to the vibrations of the carboxylate of the ionomer (Coleman et al 1990). Unlike the non-neutralized precursors, the neutralized samples exhibited absorptions in the region of $1500\sim 1700\text{ cm}^{-1}$. In the EMAA4-Zn samples, only one peak at 1585 cm^{-1} was

observed which corresponded to the asymmetric carboxylate stretching vibration of the tetrahedral structure of the tetracoordinated zinc carboxylate multiplet while in EMAA15-Zn samples, along with peak at 1585 another peak around 1620 cm^{-1} assigned to an acid salt structure were observed (Coleman et al 1990).

Table 2.2 Characterization of synthesized EMAA-Zn ionomers

Type of ionomer	$n_{1/2\text{ZnO}}/n_{\text{MAA}}$ ¹	ZnO content (wt%)	Theoretical degree of neutralization ² (%)	Degree of Neutralization determined using FT-IR (%)
EMAA15-Zn	0	0	0	0
	0.25	1.45 ± 0.02	21	25 ± 4
	0.5	3.25 ± 0.16	47	41 ± 6
	0.75	4.66 ± 0.07	69	48 ± 2
	1	5.41 ± 0.14	81	60 ± 10
EMAA4-Zn	0	0	0	0
	0.25	0.29 ± 0.09	15	24 ± 6
	0.5	0.70 ± 0.06	37	31 ± 8
	0.75	1.21 ± 0.07	65	38 ± 8
	1	1.51 ± 0.18	81	51 ± 5

¹ Molar ratio of initially added ZnO and MAA during melt processing in order to obtain certain degree of neutralization according to the MAA content of EMAA-H used.

² Theoretical degree of neutralization was calculated based on the actual ZnO content incorporated in the preparation of EMAA-Zn, which was determined by TGA analysis of the compound and was assumed to be completely consumed by EMAA-H.

Table 2.2 shows the ZnO content in EMAA-Zn ionomers based on the residual weight percentage obtained from TGA test. From that a theoretical degree of neutralization can be calculated by assuming all the ZnO in the residues come from zinc carboxylate in the ionomers. The difference between degree of neutralization determined from FT-IR and theoretical ones from TGA perhaps was due to non-completed neutralization.

2.3.2 Mechanical properties

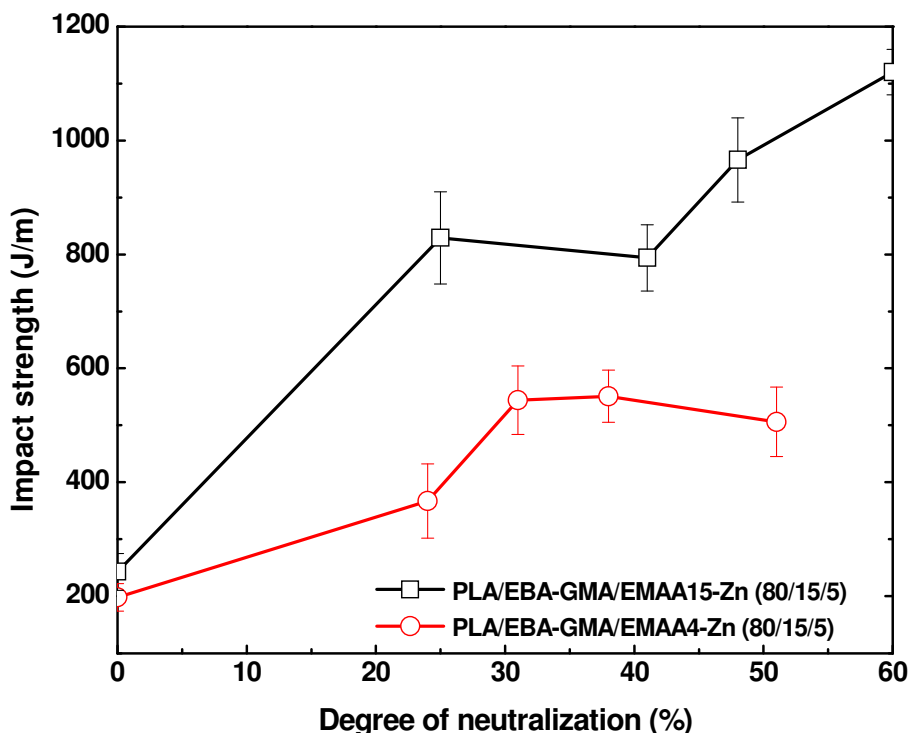


Figure 2.3 Effect of degree of neutralization of the EMMA-Zn ionomer on impact strength of PLA/EBA-GMA/EMAA-Zn (80/15/5, w/w/w) blends.

Figure 2.3 shows the effects of degree of neutralization of EMMA-H with different MAA content (4 wt% vs. 15 wt%) on the impact properties of the blends. As a control, both of ionomer precursors (i.e. non-neutralized EMMA-H) were also studied as an alternative to EMMA-Zn in the PLA ternary blends. In the blends containing EMMA15-H or EMMA15-Zn, the impact strength showed a rapid increment from un-neutralized samples to 25% neutralized one and then was further improved up to 1120J/m with increasing degree of neutralization. In the blends containing EMMA4-H or EMMA4-Zn, the impact strength showed improvement up to 31% of neutralization after which almost showed no changes along degree of neutralization. For all level of neutralization, the PLA blends containing EMMA15-H or EMMA15-Zn showed considerably higher impact strength compared with those modified by EMMA4-H or EMMA4-Zn. It was

found that the degree of neutralization of EMAA-H played a significant effect on notched Izod impact strength of the resulting PLA/EBA-GMA/EMAA-Zn blends. When either of non-neutralized EMAA-H copolymers ('EMAA4-H' and 'EMAA15-H') was used, the ternary blend failed to achieve the high level of impact toughness (less than 250 J/m) regardless of MAA weight in the EMAA-H copolymers used. The situation was different when partially neutralized EMAA-H was used. The ionomers derived from both EMAA4-H and EMAA15-H resulted in a remarkable enhancement of impact strength of the ternary blends (Figure 2.3), but those from the latter (containing more MAA monomer) exhibited more pronounced effect. The impact strength of the ternary blends based on EMAAH-15 and EMAAH-4 were 8 and 10 times that of neat PLA (Table 2.3), respectively. After the ionomer precursor (i.e. non-neutralized EMAA-H) was partially neutralized, a remarkable improvement of impact strength of the ternary blends was found. But for a given degree of neutralization, more remarkable improvement in the impact strength was found for the use of the ionomere derived from EMAA15-H. For example, the ternary blend containing EMAA15-Zn25 exhibited a super toughness (829 J/m), ca. 33 times that of neat PLA (25 J/m). In contrast, the ternary blends containing EMAA4-Zn24 only displayed an impact strength of 367 J/m, which was approximately 14.5 times that of neat PLA. Noteworthy, the ternary blends with EMAA15-Zn60 displayed a tremendous toughening effect with impact strength of 1120 J/m, approximately 45 times that of neat PLA prepared under same conditions. The superior impact strength of the blend containing neutralized EMAA-H relative to the ones containing non-neutralized EMAA-H was likely attributed to the improved interfacial adhesion, as revealed in the later SEM analysis. The improved compatibilization reactions between epoxy groups of EBA-GMA and terminal groups of PLA catalyzed by Zn ions were likely to be responsible for the super-toughness above (Liu et al 2010).

Table 2.3 Mechanical properties of various PLA/EBA-GMA/EMAA-Zn (80/15/5) blends prepared at 240 °C

Type of EMAA-H/EMAA-Zn	Impact strength (J/m)	Strain at break ¹ (%)	Tensile Strength ¹ (MPa)	Modulus ¹ (GPa)
neat PLA	25 ± 5	4.4 ± 0.5	68.3 ± 0.7	3.35 ± 0.14
EMAA15-H	243 ± 32	27.3 ± 3.0	35.8 ± 0.5	2.06 ± 0.08
EMAA15-Zn25	829 ± 81	24.6 ± 4.8	37.0 ± 0.1	2.12 ± 0.07
EMAA15-Zn41	794 ± 58	25.8 ± 4.0	38.4 ± 0.2	2.19 ± 0.02
EMAA15-Zn48	966 ± 74	21.8 ± 2.4	38.5 ± 0.4	2.17 ± 0.05
EMAA15-Zn60	1120 ± 40	23.5 ± 4.0	37.4 ± 0.4	2.13 ± 0.07
EMAA4-H	198 ± 24	20.0 ± 3.1	38.5 ± 0.3	2.24 ± 0.04
EMAA4-Zn24	367 ± 65	19.6 ± 1.5	38.9 ± 0.2	2.28 ± 0.03
EMAA4-Zn31	544 ± 60	20.5 ± 2.0	37.9 ± 0.1	2.19 ± 0.02
EMAA4-Zn38	551 ± 46	22.1 ± 2.4	37.6 ± 0.3	2.18 ± 0.06
EMAA4-Zn51	506 ± 61	15.8 ± 2.4	39.3 ± 0.4	2.24 ± 0.04

¹ Tensile test conducted at a rate of extension of 2 in/min.

Table 2.3 also summarizes the tensile properties and impact strengths of these ternary blends. Unlike the impact strength, tensile properties of the ternary blends were less affected by the MAA content in the ionomer precursor EMAA-H copolymers and the degree of neutralization. Like many other toughened PLA systems, due to the incorporation of flexible polymers, all blends suffered from great loss in both tensile and modulus as compared to that of neat PLA (ca. 35 ~ 40% of reduction). But tensile strength and modulus of these ternary blends differed slightly and ranged in 35~40 MPa and 2~2.3 GPa, respectively. This suggested that the strength and modulus of such ternary blends were mainly determined by the content of PLA.

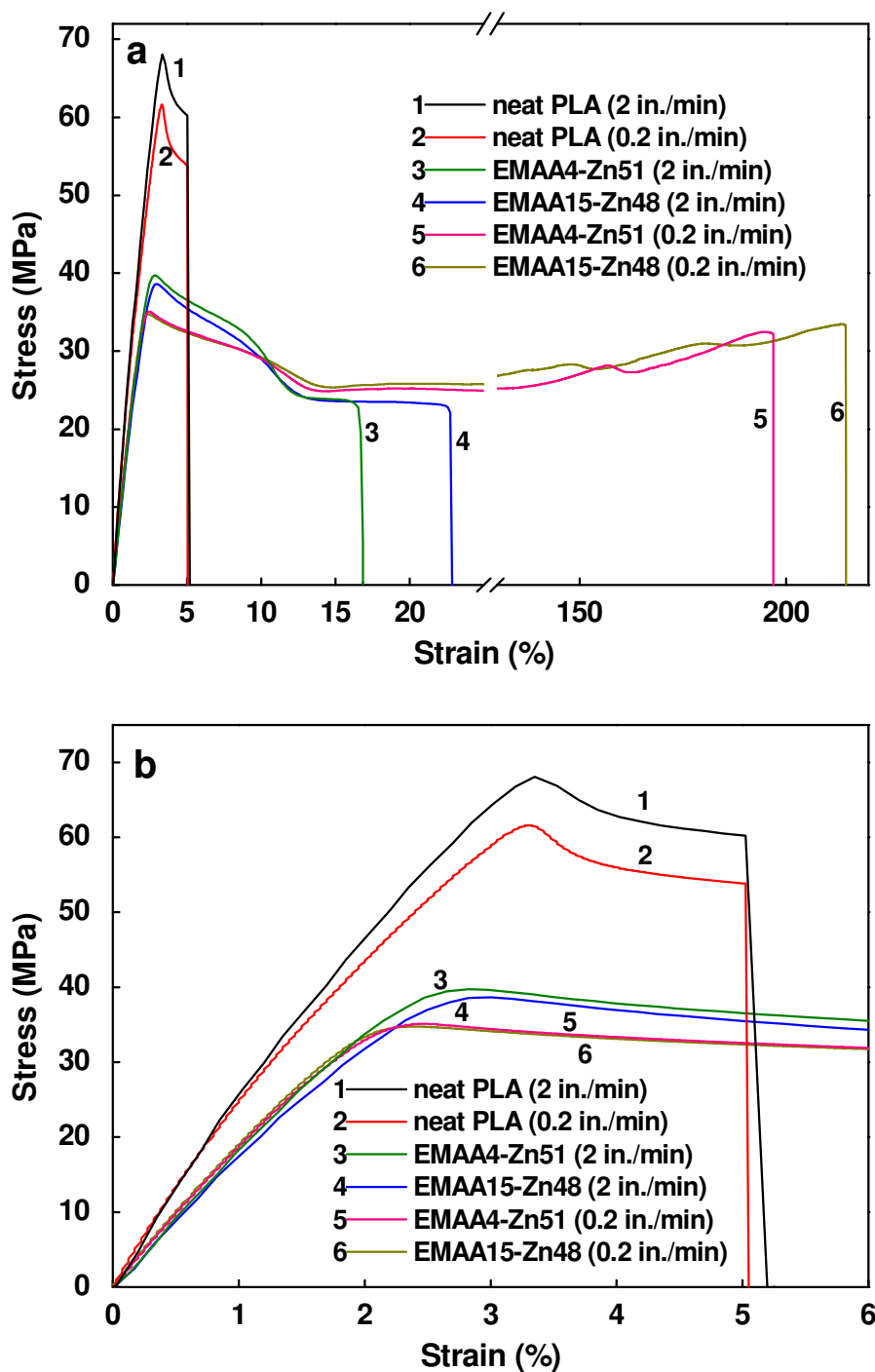


Figure 2.4 Tensile stress-strain curves of neat PLA and the PLA/EBA-GMA/EMAA-Zn (80/15/5, w/w/w) blends prepared at 240°C with different EMAA-Zn ionomers added under fast (2 in/min) and slow (0.2 in/min) testing rate, respectively. a. stress-strain curves until material fracture; b. details of the stress-strain curves in the neighborhood of yield points.

Figure 2.4 shows the stress-strain curves of the neat PLA and two PLA/EBA-GMA/EMAA-Zn ternary blends under fast (2 in/min) and slow (0.2 in/min) rates of extension, respectively. Neat PLA displayed a brittle behavior in the tensile test as the specimens quickly broke after it passed the yield point, being irrelevant to the strain rate of test. It was apparent that the incorporation of EBA-GMA and EMAA-Zn into PLA resulted in drastic improvement in tensile toughness. The strain-at-break increased considerably compared with that of neat PLA. However, both tensile modulus and yield strength decreased compared with that neat PLA. In both PLA ternary blends, higher strain rate of test led to higher yield strength and much lower strain-at-break and little change in modulus. However, both the yield strength and strain-at-break did not show significant difference when different zinc ionomer were used. Similarly, no apparent change in the modulus was observed when different types of ionomers were used.

2.3.3 Morphology of fracture surfaces

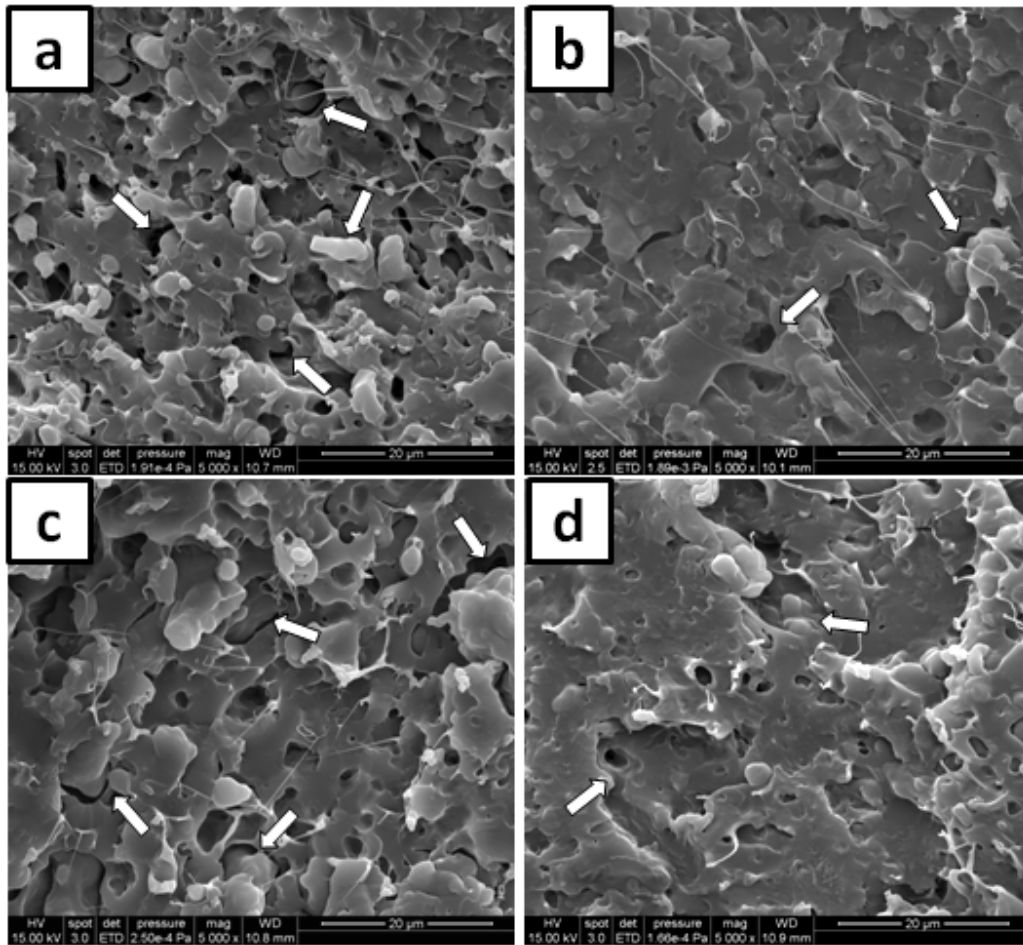


Figure 2.5 SEM images of room temperature impact fracture surfaces of PLA ternary blends adjacent to the notch with different EMAA-H or EMAA-Zn ionomers: (a) EMAA4-H; (b) EMAA4-Zn51; (c) EMAA15-H; (d) EMAA15-Zn60.

The investigation on impact-fractured surfaces of the ternary blends in the vicinity of the notch was performed in terms of SEM and the morphological results of some typical blends are exemplified in Figure 2.5. It was noted that the neutralization of EMAA had a pronounced effect on the interfacial adhesion of the blends. In the fracture surfaces of the ternary blends with EMAA4-H and EMAA15-H (Figure 2.5a and 2.5c), the dispersed phase appeared as smooth droplets in the matrix and the holes left at impact-fractured surfaces were smooth and lacked of perceptible plastic deformation. This observation suggested insufficient interfacial adhesions and

the debonding was relatively easy. When the EMAA4-Zn51 ionomer was used, i.e. for the PLA/EBA-GMA/EMAA4-Zn51 (80/15/5 w/w/w) ternary blend, improved wetting of the EBA-GMA droplets by PLA was noticeable and obvious plastic deformation of adjacent matrix was noted at the impact fractured surface (Figure 2.5b). When the EMAA15-Zn60 ionomer was used, wetting of the rubber droplets was also significantly enhanced compared to that when EMAA15-H was used and massive plastic deformation was evident at the fracture surface (Figure 2.5d). The majority of the particles were well attached to the PLA matrix, suggesting an increase of the interfacial adhesion between the two phases. The better wetting of the dispersed phase probably indicated the increased interfacial reactions between PLA and EBA-GMA under the catalysis of Zn ions. This morphological observation was in correspondence with the impact properties of these blends.

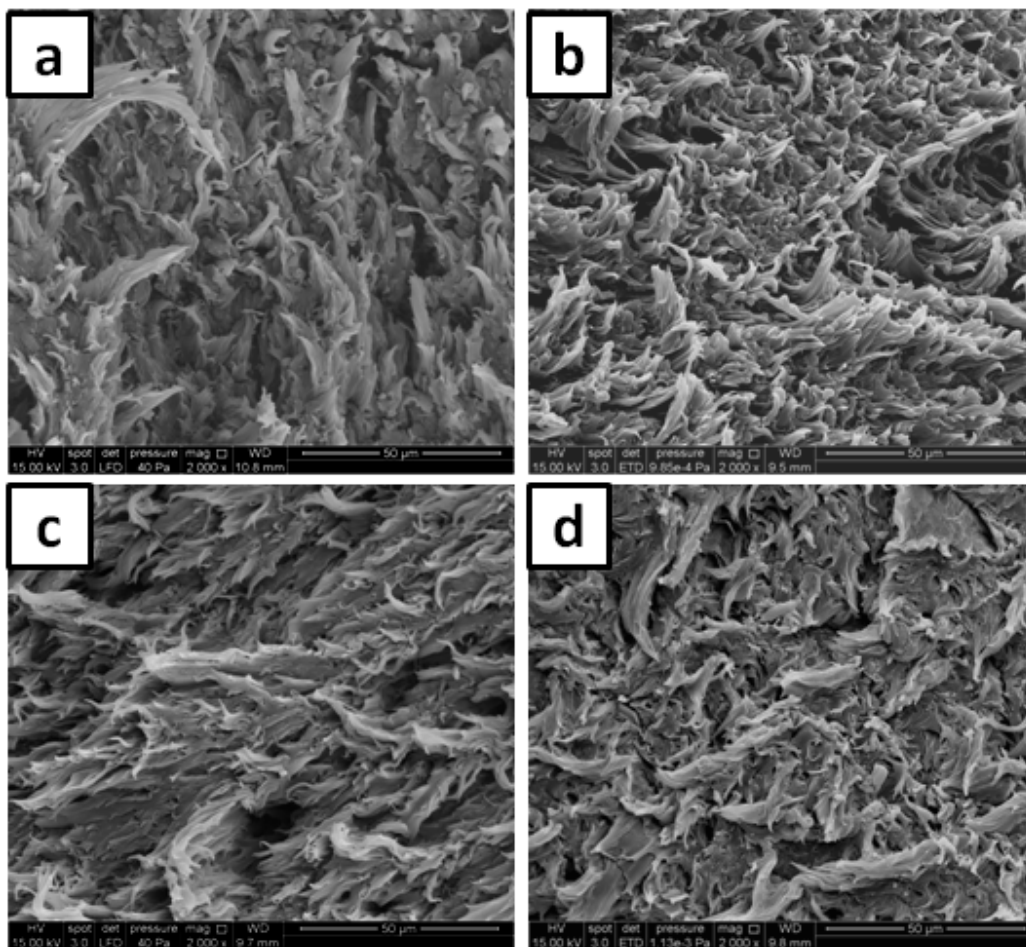


Figure 2.6 SEM micrographs of tensile-fractured surface of PLA/EBA-GMA/EMAA-Zn blends under different rate of extension: (a) EMAA15-Zn48 (0.2 in/min); (b) EMAA15-Zn48 (2 in/min); (c) EMAA4-Zn51 (0.2 in/min); (d) EMAA4-Zn51 (2 in/min).

Figure 2.6 shows the SEM micrographs of the tensile fractured surfaces of the PLA/EBA-GMA/EMAA-Zn blends under different rate of extension. Fibrillation of the matrix resulted from shear yielding was observed in all the blends under either high (2 in/min) or low (0.2 in/min) crosshead speed. These fibrillous appearances indicated that plastic deformation took place in the matrix of the blends during tensile test. Extensive shear yielding of the matrix resulted from the cavitation of particles was observed in both blends with EMAA15-Zn48 and EMAA4-51 when the rate of extension was lower. The level of matrix shear yielding decreased when the rate of extension was high. On some spots of the tensile fracture surfaces, the matrix

shear yielding of the blends (Fig. b, d) is limited. Using different zinc ionomers in these PLA ternary blends did not show significant influence on the fibrillation of matrix during tensile testing. These SEM morphologies from the tensile fractured surfaces agreed with that of tensile elongation and tensile strength of the blends. It can be concluded that cavitation of elastomer and the shear yielding of the matrix are responsible for the improvement in tensile toughness of the PLA ternary blends.

2.4 Conclusions

The effects of MAA content in EMAA-H precursors and their neutralization degree on mechanical properties and fracture morphologies of the resultant ternary polymer blends were investigated. The maximum impact strength of the ternary blends displayed increases up to 45 times that of neat PLA. The zinc ions were found to play an essential role in achieving high toughening effect. On the basis of SEM analysis, it was found that zinc ions promoted achieving good interfacial adhesion between modifier and the PLA matrix. The SEM analysis showed a significantly improved compatibilization between PLA and EBA-GMA presumably came from the reaction between epoxy groups of EBA-GMA and terminal groups of PLA under the catalysis of zinc ions. Moderate tensile properties were possessed by all ternary blends with little difference among them. A large extent of shear yielding of the matrix was found responsible for the improvement in tensile toughness of the PLA ternary blends.

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Chapter 3 Effect of reactive compatibilization and crosslinking reaction on toughening of PLA/EBA-GMA/EMAA-Zn ternary blends

ABSTRACT

In the reactive blending of PLA, EBA-GMA and EMAA-Zn (or EMAA-H), interfacial compatibilization and crosslinking reaction were simultaneously involved. The effect of those two reactions on interfacial adhesion, crosslinking degree of rubber, blend morphologies and the substructure of dispersed particles in the PLA/EBA-GMA/EMAA-Zn ternary blends were studied. Interfacial compatibilization reaction between the epoxy functionalities groups of EBA-GMA and the terminal hydroxyl groups of PLA was studied confirmed using Fourier transform-infrared spectroscopy (FT-IR). Crosslinking reaction of EBA-GMA was investigated by torque rheology and its crosslinking level was studied using dynamic mechanical analysis (DMA). The particle sizes of dispersed domains were analyzed using images acquired from by transmission electron microscopy (TEM). Zinc ion in EMAA-Zn was found to catalyze both the interfacial compatibilization reaction and the crosslinking reaction of EBA-GMA, and the methacrylic acid (MAA) content and the degree of neutralization of zinc ionomer were found to have an influence on the extent of both reactions. Consequently, the ionomer used had an effect on the interfacial property, cavitation resistance, and the particle size of dispersed domains, three of which are the most important parameters determine the final impact strength of the blends.

Keywords: *Impact performance, reactive compatibilization, crosslinking degree, particle size*

3.1 Introduction

The brittleness of PLA limits its use in applications when toughness especially impact strength is required. This shortcoming of PLA can be overcome by blending with rubber or other flexible polymers. Among various kinds of efforts to address this issue, melt blending appears to be the most promising way to improve its toughness (Li and Shimizu 2007; Coltelli et al 2008; Todo et al 2007; Jiang et al 2006; Wang et al 2009; Zhang et al 2009; Su et al 2009; Oyama 2009; Anderson et al 2003; Anderson and Hillmyer 2004). It has been shown that reactive blending was particularly effective in improving the impact performance of PLA blends (Anderson et al 2003; Anderson and Hillmyer 2004; Oyama 2009). Even though a few supertoughened PLA blends (>530 J/m of notched impact strength (Wu 1990)) under the notched situation were reported, (Anderson et al 2003; Anderson and Hillmyer 2004; Oyama 2009) the understanding on such super-toughening mechanism is still to be clarified.

In a recent work, PLA was reactive blended with an ethylene/n-butyl acrylate/glycidyl methacrylate terpolymer elastomer (EBA-GMA) and a zinc ionomer of ethylene/methacrylic acid copolymer (EMAA-Zn) (Liu et al 2010). In the PLA/EBA-GMA/EMAA-Zn blends, two reactions occurred simultaneously during melt-blending, namely, the vulcanization (or crosslinking) reaction of EBA-GMA triggered by carboxylic acid in EMAA-H or EMAA-Zn and the reactive compatibilization between PLA and EBA-GMA. The former reaction determined the crosslinking level of rubber phase, while the later one contributed to the interfacial compatibilization between PLA matrix and modifiers. The morphological parameters of the blends were affected by both the reactions.

It has been shown that the interfacial adhesions between dispersed particles and the matrix, crosslinking degree of rubber phase, size and substructure of dispersed particles all have an

effect on the impact performance of these blends (Liu et al 2010; Liu et al 2011). Sufficient interfacial strength is a prerequisite to achieve satisfactory toughening effect in many blend systems. Crosslinking reaction of rubbers was expected to increase their cavitation resistance due to an increase in the bulk modulus. The Predominant mechanism in blends of many polymers such as polyamide (PA) (Borggreve et al 1989), polycarbonate (PC) (Parker et al 1990), and epoxy resins (Yee and Pearson 1986; Becu et al 1997) of the improvement of toughness was found to be cavitation of the rubber particles followed by extensive shear yielding throughout the matrix. This microvoiding process can occur in different forms, e.g. interfacial debonding, single or multiple cavitation of rubber phase, with or without fibrillation, depending on the substructure of modifier particles and the physical properties of comprising materials (Dompas et al 1995; Si et al 2007). It was found that the micromechanical deformation processes depend on the substructure of the dispersed phase (Kim and Michler 1998). An effective approach to achieve high fracture toughness of polymeric blends involves a core-shell impact modifier (Ohishi 2004; Guo et al 2003), or a multiphase one (Okamata et al 1993; Yu et al 2009; Kim and Michler 1998).

In the toughened PLA/EBA-GMA/EMAA-Zn ternary blends, appropriately controlled characteristics are very important for achieving high level of impact toughness of such blends. The changes in interfacial adhesion, crosslinking level of the rubber phase, the morphological parameters and finally impact properties of the blends. Therefore, the aim of this study is to elucidate the roles of interfacial adhesion, crosslinking degree and morphological aspect of the blends on the impact performance of PLA/EBA-GMA/EMAA-Zn (or EMAA-H) ternary blends.

3.2 Experimental

Materials. The materials used in this study and some specifications are listed in Table 3.1.

Table 3.1. Characteristics of materials used in this study

Material (abbreviation)	Grade (supplier)	Specifications
Poly(lactic acid) (<i>PLA</i>)	PLA2002D (NatureWorks)	MI (210°C, 2.16kg) = 5~7 g/10min
Ethylene/n-butyl acrylate/glycidyl methacrylate copolymer (<i>EBA-GMA</i>)	Elvaloy® PTW (DuPont Co.)	MI (190°C, 2.16kg) = 12 g/10min; melting point (DSC) = 72°C; E/BA/GMA = 66.75/28/5.25 (wt%) ¹
Ethylene/methacrylic acid copolymer (<i>EMAA15-H</i>)	Nucrel® 925 (DuPont Co.)	MI (190°C, 2.16kg) = 25 g/10min; melting point (DSC) = 92°C; methacrylic acid content = 15.0 wt%
Ethylene/methacrylic acid copolymer (<i>EMAA4-H</i>)	Nucrel® 0411HS (DuPont Co.)	MI (190°C, 2.16kg) = 11 g/10min; melting point (DSC) = 109°C; methacrylic acid content = 4.0 wt%
Zinc Oxide Powder (<i>ZnO</i>)	BAKER ANALYZED® Reagent (J.T. Baker Chemical Co.)	specific gravity 5.67 g/cm ³ ; melting point = 1975°C

¹ Kaci et al 2006

The EMAA-H copolymers containing 15 wt% and 4 wt% MAA were designated as EMAA15-H and EMAA4-H, respectively. The zinc ionomers derived thereof were designated as EMAA15-ZnX and EMAA4-ZnX, respectively, in which X referred to the percentage of neutralization. For example, ‘EMAA15-Zn60’ referred to the EMAA-Zn ionomer which had 60% of the carboxyl groups of its precursor (EMAA15-H) neutralized by ZnO.

Preparations of zinc ionomers. Prior to extrusions, EMAA-H pellets were oven-dried for at least 1 day at 80 °C and zinc oxide was oven-dried for at least 1 day at 150 °C. EMAA-H pellets were manually mixed with ZnO powders prior to extrusions. Neutralization reaction for

preparing zinc ionomers, i.e. EMAA-Zn, was conducted in a co-rotating twin screw extruder (Leistritz ZSE-18) with a screw diameter of 17.8 mm and an L/D ratio of 40 at a screw speed of 50 rpm. The temperature profile of the extruder barrels was 180/190/190/200/200/200/190/180°C from the first heating zone (next to feeding throat) to die, respectively. Vacuum at the 7th zone of the extruder was applied to eliminate small molecules generated during neutralization. The extrudates were pelletized and then extruded for a second time under the same condition in order to make the neutralization reaction more thorough and uniform. Likewise, the EMAA-H pellets without an addition of ZnO was processed also under the same conditions and was used as a control.

PLA ternary blend preparation. Prior to extrusions, the PLA pellets were dried for at least 1 day at 80 °C; EMAA-H or EMAA-Zn pellets obtained in the former step were dried for at least 1 day at 75 °C; EBA-GMA pellets were dried for at least 1 day at 65 °C. For all PLA ternary blends, the PLA content was fixed at 80 wt%, while the content of EBA-GMA and EMAA-Zn (or its un-neutralized precursor, EMAA-H) was fixed at 15 wt% and 5 wt% based on the total blend weight, respectively. Melt blending was performed using the same extruder at a screw speed of 50 rpm to prepare PLA/EBA-GMA/EMAA-Zn (80/15/5, w/w/w) and PLA/EBA-GMA/EMAA-H (80/15/5, w/w/w) ternary blends. The temperature of reactive extrusion was set at 240 °C. The barrels temperature profile of the extruder was set as 210/220/230/240/240/240/230/220°C from the first heating zone (next to feeding throat) to die, respectively. Prior to injection molding, the compounds were dried at 80 °C overnight in a convection oven. Specimens for mechanical properties measurement were injection molded (Sumitomo SE50D) at melt temperature of 190 °C and mold temperature of 35 °C. After injection molding, all test specimens were conditioned at 23 °C and 50% RH for 7 days prior to

testing and characterization.

Fourier transform-infrared spectroscopy (FT-IR). The absorption spectra were recorded using a Thermo Nicolet Nexus 670 spectrometer with a resolution of 4 cm^{-1} and 32 scans. For each PLA/EBA-GMA/EMAA-Zn blend, the injection-molded blend specimen was first microtomed into slices with $\sim 120\text{ }\mu\text{m}$ in thickness, and then dissolved into 1,4-dioxane at ambient temperature under stirring for 24 hours. The as-obtained suspension was then centrifuged at 7500 rpm for 30 min to recover the insoluble solid and then washed 1,4-dioxane followed by the repeated centrifugation for 3 times in order to thoroughly remove free PLA. A very small amount of insoluble residues were grinded with dried KBr powder and then compressed into discs for FT-IR test. All FT-IR samples were oven-dried under a vacuum to eliminate the effects of residual solvent and moisture prior to testing. After the baseline correction, the deconvolution of the bands at ~ 1764 , ~ 1734 , and $\sim 1700\text{ cm}^{-1}$ was well made using the Lorentzian function.

Torque rheology. Torque rheometer (Haake Rheomix 600p) was utilized to compound at the same rotation speed and blending temperatures as extrusion processing, i.e. 50 rpm and 240°C , to study the chemical reactions during melt mixing. During the entire mixing period, the torque values were recorded as function of mixing time.

Dynamic mechanical analysis (DMA). Dynamic mechanical properties of the blends were measured with the DMA Q800 (TA Instruments) in a single-cantilever mode with an oscillating frequency of 1 Hz. The temperature was swept from -100 to 150°C at $3^{\circ}\text{C}/\text{min}$. For each sample, duplicated tests were performed in order to ensure the reproducibility of data.

Transmission electron microscopy (TEM). Ultra-thin sections of ca. 70~80 nm in thickness from the plane perpendicular to the injection flow direction were sliced using a RMC

cryo ultra microtome equipped with a diamond knife and mounted on formvar coated 200-mesh nickel grids. The sub-micro-structure of the ternary blends was studied using transmission electron microscopy (TEM, JEOL 1200 EX) at an accelerated voltage of 100 kV. For the purpose of particle size analysis, at least 700 particles were analyzed by a semi-automated image analysis technique based on NIH[®] image software. The cross-sectional area (A_i) of each individual particle (i) was measured and converted into an equivalent diameter of a sphere by the equation ($d_i=(4A_i/\pi)^{0.5}$). Weight-average particle diameter (d_w) which is usually thought to give a better correlation with notched impact toughness than number average particle diameter (d_n), (Oshinski and Paul et al 1997), (van der Wal et al 1999) was determined from the following equation:

$$d_w = \frac{\sum n_i d_i^2}{\sum n_i d_i} \quad (1)$$

where n_i is the number of particles having the apparent particle diameter d_i . Both the ratio of weight average particle diameter to number average particle diameter (i.e. d_w/d_n) and the ratio of volume average particle diameter to number average particle diameter (i.e. d_v/d_n) were used to characterize the polydispersity of particle size. The volume average particle diameter (d_v) was calculated from the following equation:

$$d_v = \frac{\sum n_i d_i^4}{\sum n_i d_i^3} \quad (2).$$

3.3 Results and Discussion

3.3.1 Reactive interfacial compatibilization

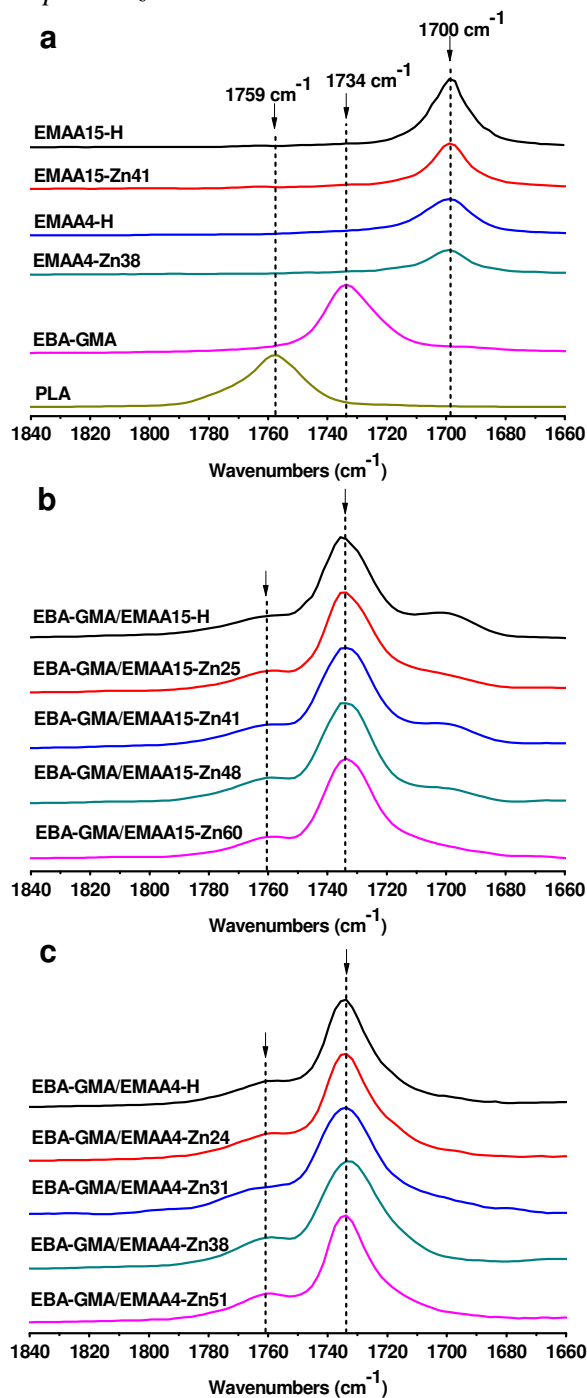


Figure 3.1 FT-IR absorption spectra in the range of 1660–1840 cm^{-1} of residues of PLA blends after the PLA matrix was dissolved by 1,4-dioxane: (a) individual polymers; (b) EBA-GMA/EMAA15-H or EBA-GMA/EMAA15-Zn; (c) EBA-GMA/EMAA4-H or EBA-GMA/EMAA4-Zn.

FT-IR was utilized to analyze the reactive compatibilization occurring at the interfaces between PLA and EBA-GMA. Figure 3.1a shows the FT-IR absorption spectra of individual polymers in the wavenumber range of 1660~1840 cm^{-1} . The absorption peak at 1759 cm^{-1} and 1734 cm^{-1} were attributed to the stretching vibration of carbonyl groups in the PLA and EBA-GMA, respectively. The EMAA-H precursors and their partially neutralized zinc-ionomer exhibited an absorption peak at 1700 cm^{-1} , which was attributed to the carboxylic acid dimer (Coleman et al 1990).

The FT-IR spectra of the insoluble residues of the PLA/EBA-GMA/EMAA-H and PLA/EBA-GMA/EMAA-Zn ternary blends are shown in Figure 3.1b and 3.1c. It was found that the absorption at around 1764 cm^{-1} was still present in the spectra of insoluble residues of all the ternary blends, suggesting that PLA probably reacted with EBA-GMA at the interfaces during melt-blending. The resulting copolymers in turn acted as an effective compatibilizer, improving the interfacial adhesion, and ultimately contributing to the impact toughness. The reaction of epoxy groups with end groups of PLA was likely to be responsible for the formation of the copolymers. Similar compatibilization reaction was also proposed in other PLA blend systems (Li and Shimizu 2009; Oyama 2009; Su et al 2009) as well as other polyester systems such as PBT (Wang et al 1997) and PET (Al-Malaika and Kong) blends, which were toughened by other kinds of epoxy-containing modifiers.

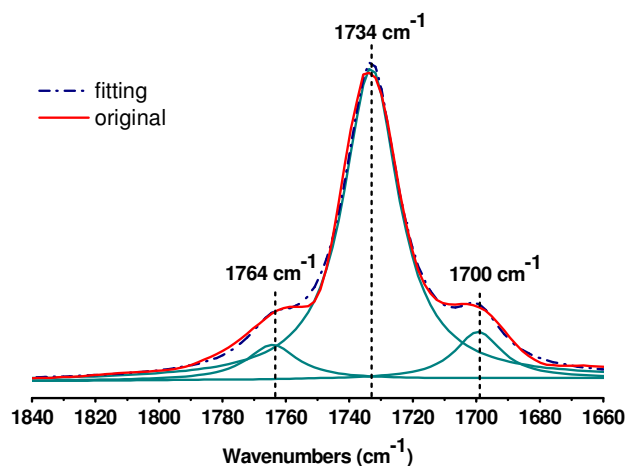


Figure 3.2 Peak-fitting result of residue from PLA/EBA-GMA/EMAA15-H blends after PLA was dissolved by 1,4-dioxane.

Figure 3.2 illustrates the peak-fitting method used to determine the location and peak area of the three peaks, ca. 1764 cm^{-1} , 1734 cm^{-1} and 1700 cm^{-1} , in the FT-IR spectrum. As shown in Figure 3.2 the spectrum obtained by peak fitting was almost identical to the original one suggesting the accuracy of the applied method.

Table 3.2 FT-IR peak-resolving data of the residues obtained from PLA/EBA-GMA/EMAA-Zn blends after PLA matrix was dissolved by 1,4-dioxane

Samples	Degree of neutralization (%)	PLA		EBA-GMA		$A_{PLA}/A_{EBA-GMA}$
						MA
Extruded PLA ¹	---	1758.2	---	---	---	---
Extruded EBA-GMA ¹	---	---	---	1733.9	---	---
PLA/EBA-GMA (80/20)	---	1762.2	2.99	1733.5	17.90	0.17
	0	1765.8	2.06	1734.0	10.61	0.19
	25 ± 4	1762.4	0.81	1733.6	4.88	0.17
EMAA15-Zn	41 ± 6	1764.6	0.91	1733.9	4.89	0.19
	48 ± 2	1763.2	1.00	1733.6	4.63	0.22
	60 ± 10	1763.9	0.88	1733.4	4.91	0.18
	0	1764.2	0.35	1733.7	2.52	0.14
	24 ± 6	1763.5	0.32	1733.1	1.90	0.17
EMAA4-Zn	31 ± 8	1765.3	0.28	1734.5	1.76	0.16
	38 ± 8	1764.1	0.23	1734.0	1.92	0.12
	51 ± 5	1763.6	0.73	1733.5	5.37	0.14

¹ Liu et al 2011

The extent of the compatibilization reaction can be approximately described by the amount of grafted PLA per unit of EBA-GMA used, as measured by the ratio of absorption peak area at 1764 cm⁻¹ to that at 1734 cm⁻¹, i.e., $A_{PLA}/A_{EBA-GMA}$. Table 3.2 summarizes the $A_{PLA}/A_{EBA-GMA}$ values of two series of the ternary blends. On the whole, the $A_{PLA}/A_{EBA-GMA}$ values remained at a comparable level regardless of neutralization degree of the ionomer used. But somewhat higher $A_{PLA}/A_{EBA-GMA}$ values were obtained from blends containing higher MAA content. This may contribute to the universally higher impact strength of PLA/EBA-GMA/EMAA15-H (or EMAA15-Zn) blends than PLA/EBA-GMA/EMAA4-H (or EMAA4-Zn). The $A_{PLA}/A_{EBA-GMA}$ values showed a maximum value at the degree of neutralization of EMAA15-H and EMAA4-H equal to 48% and 24%, respectively.

3.3.2 Crosslinking of EBA-GMA

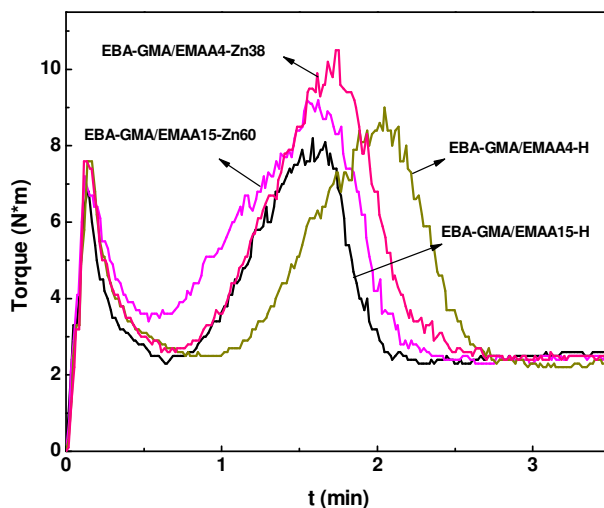


Figure 3.3 Torque vs. time for mixing of binary blends of EBA-GMA with EMAA-H and EMAA-Zn (3:1 w/w).

The crosslinking reaction of EBA-GMA with EMAA-H and EMAA-Zn during melt blending was monitored using a Haake torque rheometer. In reactive blending, as the reactions (e.g. crosslinking) between components proceeds, the corresponding changes in molecular structures of polymers inevitably result in the variation of rheological properties. If the reactions are extensive enough, the change of viscosity in the melt can be conveniently detected using a torque rheometer. As crosslinking of rubber takes place, the viscosity of the melt will increase; therefore crosslinking of rubber with time can be conveniently measured using a torque rheometer.

Figure 3.3 shows torque evolution as a function of mixing time for the binary blends of EBA-GMA with different EMAA-H (or EMAA-Zn) at a fixed weight ratio of 3:1. The initial sharp and strong peak was attributed to the melting of the pellets. The subsequent rise in torque after melting was due to the occurrence of the crosslinking reactions of EBA-GMA (Liu et al 2010). The slope of torque rise with mixing time was indicative of the rate of crosslinking reaction, while the maximum torque value indicated the intensity of crosslinking reaction. The

onset time of crosslinking reaction can be defined as the time period from the point that polymers start melting to the point the rubber starts crosslinking. The onset time indicated that EMAA15-H caused more rapid crosslinking of EBA-GMA than EMAA4-H. This result suggests that more carboxylic acid groups in the EMAA-H precursors contributed to accelerating the crosslinking reaction of EBA-GMA. After EMAA4-H precursor was partially neutralized by ZnO, the crosslinking reaction of EBA-GMA became faster in term of shortened onset time, and the maximum torque was enhanced as well. When EMAA15-H precursor was partially neutralized, increased maximum torque values was observed and the curve did not show significant shift. This result reveals that a zinc ion in EMAA-Zn was likely to act as a catalytic role in the crosslinking reaction o EBA-GMA. Zn ions in EMAA-Zn ionomer are likely to activate both the ring-opening reactions of epoxy with carboxylic acid and hydroxyl group. The former reaction brings ester type crosslinks while the latter ether type crosslinks. It is interesting to note that after the torque reached a maximum, the curves did not level off but rapidly decreased instead.

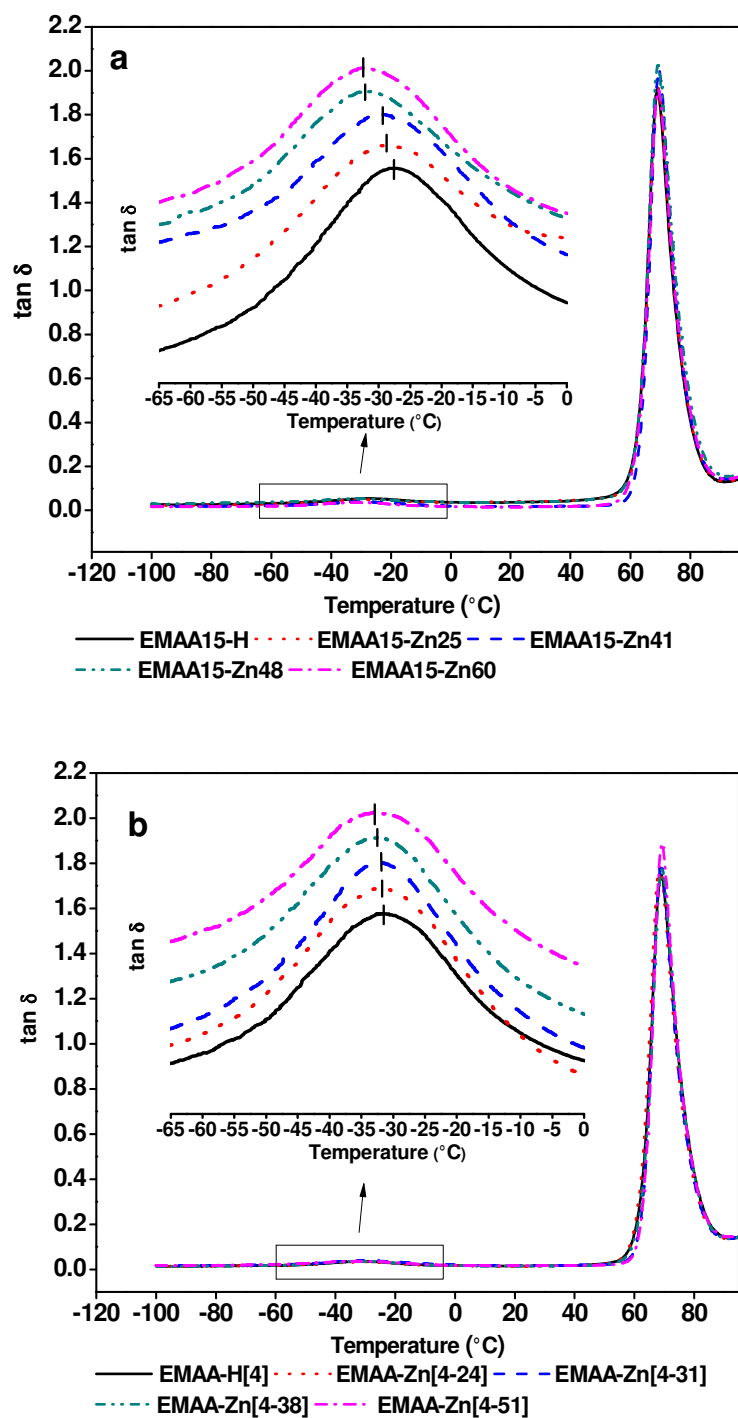


Figure 3.4 Dependence of damping factor (Tan δ) on temperature for various PLA/EBA-GMA/EMAA-Zn (80/15/5) ternary blends. Curves were shifted vertically for clarity.

Table 3.3 The changes of glass transition temperatures of the rubber phases in PLA/EBA-GMA/EMAA-Zn (80/15/5) ternary blends

EMAA15-H/EMAA15-Zn		EMAA4-H/EMAA4-Zn	
Degree of neutralization (%)	T _g of rubber phase (°C)	Degree of neutralization (%)	T _g of rubber phase (°C)
0	-27.6	0	-31.1
25 ± 4	-28.8	24 ± 6	-31.7
41 ± 6	-29.6	31 ± 8	-31.8
48 ± 2	-31.9	38 ± 8	-32.2
60 ± 10	-32.4	51 ± 5	-32.6

Damping factor (Tan δ) as a function of temperature for various PLA/EBA-GMA/EMAA-H (or EMAA-Zn) blends are shown in Figure 3.4. The glass transition temperatures (T_g) of the EBBA-GMA phase in the ternary PLA blends are summarized in Table 3.3. As shown in Figure 3.4, all ternary blends exhibited two glass transition temperatures (T_g), with one peak at ca. -30 °C w being associated with the EBA-GMA phase and the other at ca. 70 °C attributed to PLA one. The T_g of the EBA-GMA phase in the PLA blends with EMAA15-H was 3.5 degree higher than that in the blends with EMAA4-H, indicating that the crosslinking degree of rubber phase was higher in the former case. As the degree of neutralization of the EMAA15-Zn ionomers increased, the T_g of the EBA-GMA phase in the ternary blends invariably shifted toward a lower temperature, indicating the gradually reduced crosslinking degree of EBA-GMA phase. However, little change in the T_g of the EBA-GMA phase was noted as the degree of neutralization degree of neutralization degree of neutralization of the EMAA4-Zn increased. In addition, no perceptible change in the T_g of the PLA matrix was noted regardless of the use of the EMAA-H or EMAA-Zn type ionomer. This result was indicative that the T_g of PLA matrix was less dependent on the degree of neutralization and MAA content of EMAA-H used.

3.3.3 Morphological parameters

It is well-known that the size and distribution of dispersed rubber particles play an important role in determining the magnitude of impact toughness and deformation mechanisms in rubber-toughened blend systems (Paul and Bucknall 2000). Therefore, the weight average particle diameter, d_w , and the distribution parameters of the particle size of dispersed phase in PLA/EBA-GMA/EMAA-H and PLA/EBA-GMA/EMAA-Zn blends with varying degree of neutralization were calculated based on TEM images of cryo-micortomed samples. Table 3.4 summarized the morphological parameters and impact toughness for all blends.

Table 3.4 Morphological parameters and impact strength of PLA/EBA-GMA/EMAA-Zn (80/15/5) ternary blends

Type of ionomer	Degree of neutralization (%)	d_w (μm)	d_w/d_n	d_v/d_n	Impact strength (J/m)
EMAA15-Zn	0	1.62	2.43	4.69	243 ± 32
	25 ± 4	1.56	2.23	4.14	829 ± 81
	41 ± 6	1.22	2.06	4.12	794 ± 58
	48 ± 2	1.33	1.87	3.84	966 ± 74
	60 ± 10	1.00	1.81	3.52	1120 ± 40
EMAA4-Zn	0	1.27	1.87	3.34	198 ± 24
	24 ± 6	0.93	1.81	3.85	367 ± 65
	31 ± 8	1.61	2.08	3.96	544 ± 60
	38 ± 8	1.18	1.80	3.00	551 ± 46
	51 ± 5	1.23	1.75	2.88	506 ± 61

The PLA/EBA-GMA/EMAA15-H blend exhibited larger dispersed domains, which was attributed to the poor adhesion between the modifier particles and PLA matrix, as evidenced by the aforesaid SEM analysis. Therefore, its impact toughness was only improved a little. However, when partially neutralized EMAA15-Zn was used, a finer dispersion of the modifier particles in the matrix was obtained. The particle size showed a decreasing trend of with increasing degree of

neutralization. Moreover, based on the results of size polydispersity (i.e. d_w/d_n and d_v/d_n), it can be seen that a better homogeneity of particle distribution was also achieved with increasing neutralization of degree. The smaller particle size probably resulted in higher level of local stress concentration which induced more shear yielding of surrounding matrix and promoted the energy dissipation process in the matrix, leading to higher impact strength. It was noted that with only a slight decrease in particle sizes from blend containing EMAA15-H to that containing EMAA15-Zn25, the improvement in impact toughness was dramatic, from ca. 200 to ca. 800 J m⁻¹ which made the blend super-toughened (>530 J/m) (Wu 1990). In the cases of blends containing EMAA4-H and EMAA4-Zn, with increased degree of neutralization up to 31%, the impact properties firstly increased first and then remain rather in the same leveled off as the EMAA4-Zn was neutralized with an increase in the degree of neutralization. No consistent trend between impact toughness and particle size was observed in this case.

3.3.4 Substructure

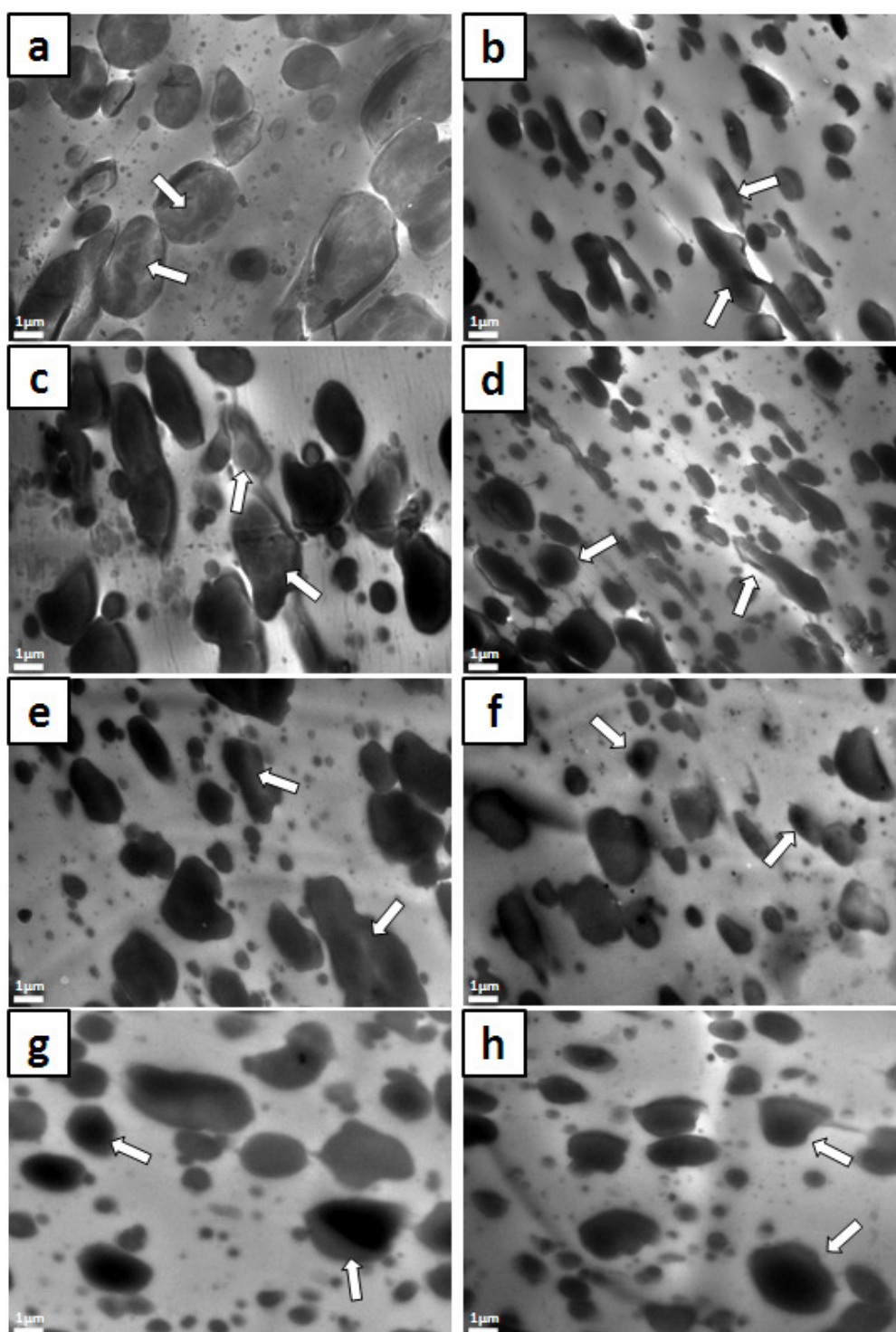


Figure 3.5 TEM images of PLA ternary blends with different EMAA-H or EMAA-Zn ionomers: (a) EMAA15-H; (b) EMAA4-H; (c) EMAA15-Zn25; (d) EMAA4-Zn24; (e) EMAA15-Zn41; (f) EMAA4-Zn38; (g) EMAA15-Zn60; (h) EMAA4-Zn51.

Figure 3.5 shows TEM micrographs of some of the PLA ternary blends. For the ternary blends containing non-neutralized EMAA-H, there are several inclusions inside almost each particle, displaying ‘salami’-like (i.e. multi-core) structure. Similar structures were also observed in some other blends as shown. It is noticeable that as the neutralization level of the ionomer increased, the number of sub-inclusions showed a decreasing trend; in both Figure 3.5g and 3.5h the dispersed phase basically turned into core-shell structure rather than ‘salami’ ones. Based on our previous studies (Liu et al 2010; Liu et al 2011), the interfacial tension between PLA and EMAA-H or EMAA-Zn was higher than that between PLA and EBA-GMA when the EBA-GMA/EMAA-Zn weight ratio was large than 1, i.e. the rubber was in excess with respect to zinc ionomer. In this case, the dispersed phase structure in which occluded ionomer inside the rubber domains is thermodynamically favorable. Therefore, the substructures were reasonably believed to be the dark EMAA-H or EMAA-Zn phase encapsulated by the grey EBA-GMA shell phase. In the ternary blends containing EMAA15-H or its EMAA15-Zn ionomers the particle size appeared to decrease with the degree of neutralization. In the blends containing EMAA4-H or its EMAA4-Zn ionomers, the particle size showed generally smaller domain sizes and the decreasing trend appeared less apparent.

3.4 Conclusions

The interfacial compatibilization reaction took place at the interfaces of EBA-GMA and PLA. At the same time the crosslinking reaction occurred within the EBA-GMA phase. The extent of compatibilization, the level of crosslinking of EBA-GMA and the morphological parameters of the blends were examined. The concentration of zinc ions, which is determined by the initial MAA content in the precursors of ionomers, has a great effect on the interfacial compatibilization. The results from FT-IR further proved that the compatibilization reaction

occurring at the interfaces of EBA-GMA and PLA and governed by the concentration of zinc ions. Effective compatibilization was found to result in smaller size of dispersed domains. The crosslinking reaction of EBA-GMA in the presence of EMAA-Zn was also monitored in terms of torque rheometer. The crosslinking degree of the EBA-GMA phases was shown in the DMA analysis and was found to be affected by both the acid content and the degree of neutralization of EMAA-Zn. Phase morphology analysis results indicated that with sufficiently good interfacial adhesion, smaller particle size was more beneficial for the blend to achieve super high impact toughness. However, with lower total functionality concentration, no clear dependence of impact performance on the particle size was noticed in this blend system. The toughening mechanism and effectiveness for the ternary blends were quite complicated and presumably resulted from the interplays between crosslinking degree and interfacial compatibilization. Good interfacial adhesion and finer dispersion of dispersed particles together with suitable crosslinking degrees seemed to be more favorable for toughening PLA. Zinc ions catalyzed the crosslinking reaction of EBA-GMA induced by the presence of carboxyl groups in EMAA-H or EMAA-Zn and hence had an effect on the crosslinking degree of EBA-GMA and may alter its physical properties. A core-shell or “salami” substructure of particles was revealed by TEM.

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Chapter 4 Summary and conclusions

The role of zinc ionomer in preparing PLA/EBA-GMA/EMAA-Zn ternary blends of high impact toughness (some of which were supertough with an impact strength > 530 J/m) was investigated. To identify the effect of zinc ions of the partially neutralized ethylene methacrylic acid (EMAA) copolymers on the impact performance of such blends, unneutralized ethylene methacrylic acid copolymers (EMAA-H), also called the precursors of ionomers, were used as controls. Two EMAA-H with initial methacrylic acid (MAA) contents of 4 wt % and 15 wt %, respectively, were chosen in this study and the EMAA-Zn ionomers derived with various degrees of neutralization were used. When the EMAA-H was used instead of EMAA-Zn, the ternary blend failed to achieve the same level of impact toughness. Furthermore, the extent of enhancement in impact toughness largely depended on the acid content and the degree of neutralization of the ionomer.

In this blend system, two important reactions were involved, i.e. interfacial compatibilization reaction between the epoxy groups of EBA-GMA and the terminal hydroxyl groups of PLA and crosslinking reaction of EBA-GMA in the presence of EMAA-Zn. These two reactions were found to be governed by the acid (MAA) content and the neutralization degree of zinc ionomers. The variations of the two involved reactions during preparation of the blends greatly influenced the morphological structure of the blends and further the final impact toughness of the PLA/EBA-GMA/EMAA-Zn (or EMAA-H) blends.

When EMAA15-H (or EMAA15-Zn) were used instead of EMAA4-H (or EMAA4-Zn), a higher degree of interfacial reaction was noted as measured by FT-IR. The SEM analysis exhibited improved wetting of the dispersed phase with the addition of zinc ionomer, indicating the catalyzing effect of Zinc ions on the interfacial reaction. The impact strength corresponded

well to the wetting of the dispersed phase by the matrix. Based on the above observations, it was concluded that zinc ions promoted the interfacial compatibilization reaction and helped the blends to achieve good interfacial adhesion between modifier particles and the PLA matrix. TEM revealed core-shell (single-core) or 'salami'-like (multi-core) substructure of the ternary blends. The substructures showed a trend of evolving from 'salami'-like structure to core-shell structure as the crosslinking degree and the particle size decreased. In the study of melt mixing of the EBA-GMA/EMAA-Zn binary blends using torque rheology, it was found that carboxylic acid groups play a more important role in the crosslinking of EBA-GMA than zinc ions. In addition, it was showed that the ionomers derived from the precursor containing low (4 wt %) MAA content, i.e. EMAA4-Zn, greatly accelerated the crosslinking reaction in term of shortened onset time and accelerated the curing rate in term of the slope of the curing portion of the torque curve. As suggested by the above mentioned results, zinc ions in EMAA-Zn catalyzed the crosslinking reaction of EBA-GMA. The crosslinking degrees of the EBA-GMA phase in the PLA ternary blends were studied by DMA. The crosslinking alters the modulus of the rubber phase hence has an effect on increasing the cavitation resistance. Increase in crosslinking degree also tends to enlarge the particle size in the final dispersion. The final blend morphology is governed by the compatibilization effect as well as the crosslinking level of elastomer. The weight average particle diameter, d_w , and the distribution parameters of the particle size of dispersed phase in the PLA ternary blends were calculated. In those blends containing EMAA15-H or EMAA15-Zn, a clear correlation between particle size and impact strength was observed. The results suggested that fine particle sizes were favorable for the optimal toughening effect. In those blends containing EMAA4-H and EMAA4-Zn, there was no apparent dependence of impact strength on particle size. This result was probably due to the limited interfacial strength. The mechanism and

effectiveness of toughening were not determined solely by any single factors discussed above. Overall, a sufficiently good interfacial adhesion, a suitable crosslinking level of rubber particles and a fine particle size within a definite range were favorable for toughening of the PLA ternary blends.

In this PLA ternary blend systems, 20% petroleum-based non-biodegradable polymers were incorporated and the biodegradability of PLA was compromised. Therefore, the development of high impact PLA blends with complete biodegradability is to be achieved in the future.