Core-shell type 충격보강제의 제조 및
PLA/충격보강제 블렌드의 특성 연구

Preparation and Characterization of Core-shell Type
Impact Modifiers and PLA/impact Modifier Blends

2012年 2月

仁荷大學校 大學院

高分子工學科

趙 南 錫
Preparation and Characterization of Core-shell Type Impact Modifiers and PLA/Impact Modifier Blends

2012年 2月

指導教授  陳 仁 柱

이 論文을 碩士學位 論文으로 提出함

仁荷大學校 大學院

高分子工學科

趙 南 錫
이 논문을 趙 南 錫 의 碩士學位論文으로 認定함.

2012年 2月

主審 ___________________

副審 ___________________

委員 ___________________
ABSTRACT

Poly(lactic acid) (PLA), well-known biodegradable polymer, is a widely used polymer which has received much attention in the last decade because it is obtained from renewable resources. It has many advantages including biodegradability, excellent biocompatibility, and low energy dependence. However, in spite of many advantages as a biomaterial, it still has several shortcomings to be used in many practical applications. Therefore, physical properties of PLA need to be improved. Blending is a simple and efficient method for improving the properties of polymers, and it has been used widely in modifying various polymers.

In this study, in order to improve the impact strength, PLA was blended with core-shell type particles, that were made up of a poly(n-butyl acrylate) (PBA) rubbery core and a poly(methyl methacrylate) (PMMA)/ethylene glycol dimeth-acrylate (EGDMA) outer shell. The core was prepared by emulsion polymerization of butyl acrylate to form PBA core latex. The particle size of the PBA core latex was decreased as the amount of the emulsifier was increased. With an increase in the emulsifier concentration the number of the micelles was increased, resulting in the reduction in the micelle size. However, the amount of the crosslinking agent did not affect the particle size. PLA/core-shell particle blends were prepared by melt blending in a Brabender mixer. The effect of the core-shell particle, in particular, the effect
of the particle size and the addition of up to 20 phr on the mechanical properties of blends was investigated by universal testing machine (UTM) and Izod impact tester. The Izod-fractured surfaces were examined by scanning electron microscopy (SEM) to study the fracture mechanism of the blends. In addition, thermal properties of blends were characterized by differential scanning calorimeter (DSC), and thermogravimetric analysis (TGA). Scanning electron microscopy and electrophoretic light scattering (ELS) results confirmed that the particles obtained indeed possessed desired core-shell structures.

Keyword: Copolyester, PLA, Biodegradable, Core-shell morphology, Impact strength, Impact modifier.
국문 요약

비분해성 플라스틱 폐기물로 인한 환경문제가 사회문제로 대두되면서 분해성 고분자 재료의 생분해성과 관련한 많은 연구가 진행되고 있으며, 특히 기존 범용 플라스틱 대체물질로 생분해성 고분자의 중요성이 학문적, 산업적 시각 모든 부문에서 크게 부각되고 있다. 바이오플라스틱은 미래 산업이라 평가 받고 있는 바이오산업과 환경산업의 핵심요소 분야로 평가되어, 인류의 환경보존과 건강증진 및 치료 그리고 석유자원의존도 탈피에 기여하는 등 사회, 경제적으로 중요한 역할을 할 것으로 판단되고 있다. 그 중 가장 유망한 합성 지방족 폴리에스터 계열중의 하나인 poly(lactic acid) (PLA)는 전문에서 얻어지는 유산을 원료로 제조되는 자연 순환의 생분해성, 생체적합성 고분자이다. 다른 생분해성 고분자와는 달리 대량 생산이 가능하고, 생체 재료와 같은 기능성 분야 뿐만 아니라 범용 고분자 재료의 기존 특성을 지니고 있어 범용 플라스틱 분야에서도 사용이 가능하다. 그러나 높은 결정화도로 인하여 물성이 brittle하여 유연성이 요구되는 조제로 응용할 경우 문제가 많이, 열안정성이 떨어 응용 가능시 급격한 분자량 감소를 유발하여 기계적 특성이 좋지 않고 가격이 높다는 단점이 있다. 또한 결정화 속도가 범용 고분자에 비해서 느리기 때문에 복잡한 산업적인 응용이 제한되고 있다. 이와 같은 단점들은 블렌딩, 공중합, 그리고 충전재의 첨가 등과 같은 방법으로 물성을 향상시킴으로써 극복할 수 있으며, 이런 방법들 중에서 가장 널리 이용되는 방법 중의 하나는 다른 고분자와의 블렌딩을 통해 물성을 향상시키는 것이다.

본 연구에서는 PLA(폴리유산)의 단점으로 지적되고 있는 brittle 한 성질을 감소시키기 위해 시판되는 충격보강제를 적용하였고, 동시에 유화중합을 통한 core-shell type PLA용 불투명 충격보강제를 개발하고 그 성능을 검토하였다. 충격보강제로는 butyl acrylate를 이용하여 poly(butyl acrylate) (PBA) core를 만든 후, methyl methacrylate, glycidyl methacrylate를
이용하여 shell 을 중합하였다. 유화중합을 이용하여 중합된 PBA core latex 는 첨가되는 유화제의 함량이 증가함에 따라 생성되는 입자의 크기가 점점 감소하는 것을 관찰할 수 있었다. 이는 용매상에 존재하는 유화제의 양이 증가함수록 micelle 의 수가 증가하면서 크기가 작아짐에 따라 생성되는 PBA core 입자의 크기가 감소되기 때문으로 판단된다. 가교제의 경우에는 첨가하는 가교제의 함량과 무관하게 입자크기는 거의 동일하였다. 실험을 통하여 시험되는 충격보강제 보다 성능이 우수한 보강제를 얻었다. 제조한 core-shell 입자의 크기와 특성을 확인하기 위하여 light scattering 과 SEM 을 이용하였으며, PLA/충격보강제 blend 의 기계적 물성을 확인하기 위해 UTM, Izod test 를 이용하였다.

Keyword: 폴리에스터 공중합체, PLA, 생분해성, Core-shell 구조, 충격강도, 충격보강제
# CONTENTS

ABSTRACT ..................................................................................................................i

CONTENTS..................................................................................................................v

LIST OF TABLES ........................................................................................................vii

LIST OF FIGURES .....................................................................................................vii

1. INTRODUCTION .................................................................................................1

2. EXPERIMENTALs .............................................................................................7

   2.1. Materials ........................................................................................................7

      2.1.1. Synthesis of core-shell latex particles .................................................7

      2.1.2. Preparation of PLA/core-shell particles blend ...............................8

      2.1.3. Preparation of PLA/commercial impact modifier blend ..............8

   2.2. Characterization ............................................................................................9

      2.2.1. Tensile strength measurement ............................................................9

      2.2.2. IZOD test ..............................................................................................9

      2.2.3. Particle morphology ...........................................................................10

      2.2.4. TGA analysis .......................................................................................10

      2.2.5. DSC analysis .......................................................................................10

      2.2.6. Particle size distribution ......................................................................11

3. RESULTS AND DISCUSSION ........................................................................12

   3.1. The ELS results of copolymer .................................................................12

   3.2. Morphology of core-shell particle ............................................................12

   3.3. Mechanical properties of PLA/core-shell blends ...............................13

   3.4. Morphology of impact modifier fractured surface ..............................14

   3.5. Thermal stability of PLA/core-shell blends .........................................14

   3.6. Mechanical properties of PLA/various impact modifier ....................15

   3.6. Morphology of fractured surface ............................................................16
LIST OF TABLES

Table 1. Recipe for core-shell emulsion polymerization.
Table 2. Tensile strength of neat PLA and PLA/commercial impact modifiers blend
Table 3. Elongation at break of neat PLA and PLA/commercial impact modifiers blend
Table 4. Impact modifier of neat PLA and PLA/commercial impact modifiers blend

LIST OF FIGURES

Figure 1. Schematic diagram of core-shell particle preparation set-up.
Figure 2. Particle size distribution of the final core-shell emulsion particle.
Figure 3. Scheme of the core-shell particle containing polyacrylate emulsion.
Figure 4. SEM images of the core-shell particles (a), (b) without EGDMA and (c) – (f) with EGDMA.
Figure 5. Impact strength of the PLA/core-shell particle blends (a) – (c) without EGDMA and (d) – (h) with EGDMA.
Figure 6. Tensile strength of the PLA/core-shell blends (a) – (c) without EGDMA and (d) – (h) with EGDMA.
Figure 7. Young’s modulus of the PLA/core-shell blends (a) – (c) without EGDMA and (d) – (h) with EGDMA.
**Figure 8.** Elongation at break of the PLA/core-shell blends (a) –(c) without EGDMA and (d) –(h) with EGDMA.

**Figure 9.** Morphology of impact fractured surface( various impact modifier).

**Figure 10.** Thermogravimetric analysis of the PLA/core-shell blends with EGDMA.

**Figure 11.** Glass Transition Behavior of PLA/core-shell Blends with EGDMA.

**Figure 12.** Tensile strength of the PLA/ various impact modifier blends.

**Figure 13.** Elongation at break of the PLA/ various impact modifier blends.

**Figure 14.** Impact strength of the PLA/ various impact modifier blends.

**Figure 15.** SEM images of Izod-fractured surface of the PLA/core-shell blends.
1. INTRODUCTION

Over the past hundred years, research and development of synthetic polymers has enabled numerous societal and technological advancements. Production of polyethylene, polypropylene, and related resins is a greater than 100 billion pound per annum industry in the United States\textsuperscript{1,2}, and these materials are increasingly employed as alternatives to glass and metal in applications ranging from drinking bottles to automotive parts. As the field of polymer science matures, many challenges still exist, one of which is the issue of sustainability and environmental impact. Due in part to a growing emphasis on “green” chemical processes, there has been increasing interest in the development and utilization of more environmentally benign polymeric materials. This classification can describe a continuum of polymers, ranging from those that are obtained from annually renewable feed stocks, to those that ultimately degrade to benign by-products after their useful lifetime\textsuperscript{3-5}.

In recent years considerable attention has been paid to biodegradable polymers, mainly owing to preservation of environment and substitution of petrochemical polymers\textsuperscript{6}. These materials and obtained from low cost and renewable resources. In addition, life cycle assessment of biodegradable polymers provide low negatively impact to environment. These properties make agricultural products the preferred raw materials over the resource limited petroleum for the manufacture of consumer products. Nearly all agricultural raw materials have the potential to be used in the manufacture of consumer
products, ranging from automobiles to utensils.

Examples of agricultural-based raw materials being pursued for various applications include vegetable oils (e.g. lubricants), fibers (e.g. composites for automotive), starches (e.g. biodegradable polymers) and cellulose (e.g. bioplastics). The conversion of agricultural-based raw materials into consumer products, however, is not straight forward. In spite of their abundance, low cost, environmental friendliness, and lack of toxicity, agricultural products lack certain properties that are critical for the manufacture of useful consumer products. For example, agricultural raw materials generally have poor water-resistance, poor oxidative stability, and poor bio-resistance. Thus, successful conversion of agricultural-based raw materials into viable consumer products requires overcoming these and other shortcomings.\(^7\)\(^-\)\(^9\) One of the possible solutions to reduce the environmental pollution caused by the plastic wastes is to replace the commodity polymers with the biodegradable polymers such as PLA, Poly(butylene succinate) (PBS), poly(glycolide) (PGA), poly(\(\varepsilon\)-caprolactone) (PCL)\(^10\).

Among various biodegradable polymers, Poly(lactic acid) (PLA), \((-\text{O(CH}_3\text{CHCO})_n\)\(^11\), is a kind of aliphatic polyester. Development of PLA was initiated with the lactide production formulas published by Bischoff and Walden in 1893. In 1932, Carothers and coworkers produced low molecular weight PLA.

Lactic acid can be produced by chemical processes or by fermentation. There are several possible routes for the production by chemical processes. Also, lactic acid is the smallest chemical molecule with an asymmetric carbon and therefore exists in two optical-isomers;
the $L$ (+) and the $D$ (-).


Unfortunately, the broad substitution of commodity plastics by PLA is limited by its brittleness behavior under impact loads14. In order to overcome this drawback, many research works has been done, for example15. Among above methods, the most widely used to modify the properties of PLA resins is to make blends as it is relatively simple and cost-effective in comparison with copolymer synthesis. The important factor in consideration of polymer blends is miscibility of blend components. It can be determined from glass transition temperature ($T_g$) of the blend compared to the $T_g$s of each components in the blend16,17. Also miscibility can be influenced by various factors such as morphology, crystalline phase, intermolecular interaction, and reduction of surface tension18. PLA can be finally biodegraded into
carbon dioxide and water through biodegradation mechanisms which have resulted from complex factors such as enzymatic, hydrolytic, or microbial\textsuperscript{19}. Because PLA has unique properties such as biodegradability, biocompatibility and good mechanical properties, it has been applied for biomedical and food packaging applications\textsuperscript{20-25}. Its degradation rate depends on the PLA crystallinity, molecular weight, molecular weight distribution, morphology, water diffusion rate into the polymer, and the stereoisomeric content\textsuperscript{26}. The slow degradation rate leads to a long \textit{in vivo} lifetime\textsuperscript{27}. There have been reports of a second surgery almost 3 years after implantation to remove a PLA-based implant\textsuperscript{28}. The slow degradation rate is a serious problem with respect to disposal of consumer commodities as well. PLA has some drawbacks, such as brittleness, low crystallization rate and low impact strength. Thus it is used in its limited applications\textsuperscript{29}.

DuPont has commercialized Biomax\textsuperscript{®} Strong PLA additives to improve toughness without significant transparency loss. These additives are designed to have ‘special chemistry’ for PLA, so even small amounts (1–5 wt\%) provide significant toughness benefits. NatureWorks LLC studied different commercial toughening agents for PLA. In their work, Blendex\textsuperscript{TM} 338, an acrylonitrile–butadiene–styrene terpolymer containing 70\% butadiene rubber, was found to significantly improve notched Izod impact strength and elongation at break of PLA. Since the idea of “particle design” was put forward by Okubo in 1980s, where the control of micro-phase separated structure of latex particles via controlling the distribution of hetero-functional groups in their internal particles or on their surface were the main focus, various latex
particles with different morphology, such as double or multi-layers structures, were obtained via specially macromolecular designing and emulsion polymerization techniques. It was found that the composite latexes were also possessing distinguished physical properties. The physical properties of latex polymer, such as Young’s modulus, tensile strength, elongation at break and solvent resistance, are very important criteria to determine its practical applications. These physical properties are closely depending on the macromolecular structure, the molecular weight, molecular inter- and intra- chemical crosslinking network structure, the size and morphology of the latex particles. The polyacrylate-based latexes are kinds of industrious latexes being widely used due to their excellent anti-oxidation, oil resistance properties. However, their physical properties including film’s toughness, light fullness, water and solvent resistances are relatively weaker, and because of this, their practical utilizations are limited. In order to improve the actual performance of acrylate-based latexes, various kinds of techniques including emulsion polymerization, latex particle design with core-shell structure and chemical modifications with silicon and fluorine related compounds are intensively developed. Particularly, there were not only a lot of research works concerning the syntheses and characterizations of the latexes with core-shell structures, but also there exist many reports related to the blends of water soluble epoxy resin with acrylate based latexes. Core-shell emulsion polymerization is a new polymerization technology based on seed emulsion polymerization. An emulsion particle with multilayer heterogeneous structures were
synthesized through the control of polymerization processes while different properties of each layer were obtained by changing the monomer. Compared to traditional common emulsion polymerization, the seed emulsion polymerization can structure architecture.

In this article, the acrylate copolymer emulsion with core-shell structure was synthesized by a seed emulsion polymerization method, in which methylmethacrylate (MMA) and butyl acrylate (BA) were used as main monomers and ethylene glycol dimethacrylate (EGDMA) as monomers and ammonium persulfate and sodium bisulfite redox system as the initiator. Two stages seeded semi-continuous emulsion polymerization were employed for constructing a core-shell structure with P(MMA-co-BA) component as the core and P(latex-co-EGDMA) component as the shell. The acrylate copolymer emulsion with core-shell structure was synthesized by a seed emulsion polymerization method, in which MMA and BA were used as main monomers (Figure 1.) For this purpose, a series of acrylic core–shell polymers were synthesized via seeded semi-continuous emulsion polymerization, and the thermal properties of blends were characterized by DSC and TGA, and morphology was investigated using SEM. The effect of the modified PLA/core-shell on the mechanical properties of blends was investigated by UTM and Izod impact tester. The Izod-fractured surfaces were examined by SEM to study the fracture mechanism of the blends.
2. EXPERIMENTAL

2.1. Materials

MMA, BA and EGDMA were obtained from Sigma-Aldrich and used as received. Then, deionized water, dried over CaCl2 overnight, then distilled. The emulsifier mixture system that was composed of sodium lauryl sulfate (SLS) as anionic emulsifier was purchased from DUKSAN PURE CHEMICALS. Co., LTD. Potassium persulfate (KPS) was obtained from DAE JUNG Chemical. PLA (Injeo 2002D) pellets for compounding were a kind gift from NatureWorks LLC, USA. Various impact modifiers were purchased from LG CHEMICALS. Co., LTD.

2.1.1. Synthesis of core-shell latex particles

The latex particles with a core-shell structure were prepared via a seeded semi-continuous emulsion polymerization. All the experiments were carried out in a 500 ml three-necked flask equipped with a mechanical stirrer, nitrogen inlet tube and feed inlet tube. The detailed recipes used were listed in Table 4. Specifically, 100 g of distilled water was first charged into the flask, the pre-emulsified monomers used as the core component together with small amount of initiator was added to the flask. 30 min later, the remaining core component was added dropwise to the reactor within 180 min. The system was kept at 80°C for additional 180 min to allow further polymerization. Then, the pre-
emulsified monomer to be used as the shell component was slowly added to the reactor within 3 h. Upon completing the addition, the system was continuously maintained polymerization was continued at 80°C for 3 h. All polymerization was carried out under a nitrogen atmosphere. After polymerization, the mixture was allowed to cool down to room temperature and then the copolymer was dried under vacuum.

2.1.2. Preparation of PLA/core-shell particles blend

In order to prevent any potential hydrolytic degradation of the biodegradable polymer during melt processing, core-shell were dried in the vacuum oven at 60°C for 48 h before melt processing. PLA/core-shell particle blends were prepared by twin-screw extruder with a screw diameter of 19 mm and a die diameter (L/D) ratio of 40. The twin screw extruder was independently operated with eight different temperature zones of respective temperature range from 170 °C to 190 °C, feeding zone at 160 °C and die section at 200 °C with the screw speed of 150 rpm. The melted samples were quenched in water bath and pelletized.

2.1.3. Preparation of PLA/commercial impact modifier blend

In order to prevent any potential hydrolytic degradation of the biodegradable polymer during melt processing. PLA/Impact modifier blends were prepared by twin-screw extruder with a screw diameter of
19 mm and a die length/die diameter (L/D) ratio of 40. The twin screw extruder was independently operated with eight different temperature zones of respective temperature range from 170 °C to 190 °C, feeding zone at 160 °C and die section at 200 °C with the screw speed of 150 rpm. The melted samples were quenched in water bath and pelletized.

2.2. Characterization

2.2.1. Tensile strength measurement

Tensile strength and Young’s modulus were measured under uniaxial elongation at room temperature in accordance to ASTM D638 by using universal testing machine (UTM, Hounsfield Test Equipment) at 20 °C and at 30% humidity. The cross-head speed was set at 50 mm/min for of the dumb-bell samples. At least 5 specimens of a given sample were measured and averaged for the tensile property. Each sample was provided with as a dog-bone type and the resulting value was at least an average of at least five measurements.

2.2.2. IZOD test

Notched Izod test (QMESYS QM 700A) of blends was performed in accordance to the ASTM D256 at room temperature. The pendulum velocity was 3.5/m/sec, and the hammer was 9.8/J. The notch was milled to have a depth of 2.54 mm, and angle of 130 °C, net weight of
65 kg. The Izod impact strength was an average of five measurements per sample.

2.2.3. Particle morphology

The polished surfaces were etched in toluene at 25 °C for 2 h to remove the MB phase. Fracture surfaces were observed by using field emission scanning electron microscopy (FE-SEM, S-4300SE, Hitachi, Japan) at an accelerating voltage of 15 kV.

2.2.4. TGA Analysis

Thermogravimetric analysis (TGA, TA instruments, Q-50) was used to study thermal stability. Samples of approximately 10 mg were heated to 750 °C with a heating rate of 10 °C/min under nitrogen gas flow with a flow rate of 20 mL/min.

2.2.5. DSC Analysis

Thermal transition was measured by using the DSC (Perkin Elmer, Diamond DSC) under nitrogen atmosphere at a heating rate of 10 °C/min. DSC was calibrated using indium as the standard, and the sample weight was maintained at 7.0 ± 0.1 mg. The thermal history of the products was removed by scanning them from 25 to 220 °C at a heating rate of 10 °C/min, and the specimen was cooled to 25 °C using scan rates of 10 °C/min.
2.2.6. Measurement of particle size distribution

In order to determine electro-phoretic properties, the zeta potential was investigated by electro-phoretic light scattering (ELS, Photal ELS-8000, Otsuka, Japan). A charge control agent was also added into the suspension of synthesized nanoparticles in the dielectric medium so as to improve their mobility. The density of the fabricated particles was measured by a gas pycnometer.
3. RESULTS AND DISCUSSION

3.1 The ELS Results of Copolymer

Table 1 shows the particles size of the core emulsion and the core-shell emulsion determined by ELS. Figure 2(a) shows the size distribution of both BA particles and BA-MMA core-shell particles. The average particle size of the core-shell emulsion (620 nm) is bigger than that of the core emulsion (572 nm). Figure 2(b) shows that the particle size of the core-shell emulsion (898.5 nm) is bigger than that of the core emulsion (751 nm) but their particle size distribution was similar. These results indicated that the narrow size distribution of the resulting emulsions and the shell monomers were polymerized on the outer layer of the core phase during the shell polymerization. Thus the designed emulsion with core-shell structure was formed (Figure 3).

3.2 Morphology of core-shell particles

Figure 4 shows the SEM micrographs of the core-shell particles containing polyacrylate emulsion. As mentioned above, the shell phase was composed of PMMA copolymer, and the core phase was composed of butyl acrylate polymer. Depending on the MMA content and the number of layers, different particle morphology was obtained. Figure 4(e) and 4(f) show the spherical core-shell particles.
3.3 Mechanical properties of PLA/core-shell blends

The impact properties of PLA blends are very important for the end use. Factors that affected to impact strength and brittle ductile transition in rubber toughened plastics blends are content of impact modifier and ratio of core–shell component. Figure 5 shows the relationship between impact strength of blend and content of BA-MMA particles. Neat PLA has impact strength of 2.1 ± 0.09. As content of BA-MMA particles increased in the blends, impact strength increased. The toughness value is poor. The smallest increase was seen with addition of #1-1st_MMA10–#2-2nd_MMA10. The highest impact values for blends in this study were 18.22±0.07 kgf-cm/cm, which were obtained for #2-3rd_MMA5 composition. Figure 6 shows the tensile properties. When the core-shell content was 20 wt%, the tensile strength and Young’s modulus. (Figure 7) of the PLA/Core-shell blends were decreased by 30% and 22%, respectively, compared to neat PLA. This was due to the fact that the core-shell particles had high modulus and tensile strength. At the interface of the core-shell particles and the PLA matrix, a thick gradient layer could be formed and provide an effective bridge for the matrix to pass the stress to the core-shell particles. The elongation at break (Figure 8) of the blend containing 20 wt% of core-shell was 47%, indicating a 10 fold increase compared to neat PLA. The results of mechanical testing showed that blends of PLA with BA-MMA particles significantly increased impact strength but slightly reduced tensile strength and tensile modulus. It should be noted that the impact strength of BA-MMA particles was greater than the commercial ones.
3.4 Morphology of impact fractured surface

SEM images of the notched impact fractured surfaces of neat PLA and PLA/Core-shell blends are shown in Figure 9. It can be seen that the edges of unfilled PLA are very smooth (Figure 9 (a) and 9(b)). Figure 9(c) – 9(f) In the case of core-shell blends are uniformly distributed in the PLA matrix, and their surface is very rough. Moreover, evident cavitation caused by debonding and stress whitening near the notched tip due to crazing/microcracks resulted. Although debonding absorbs a considerable amount of fracture energy.

3.5 Thermal stability of PLA/core-shell blends

Figure 10 shows the thermal degradation curves of PLA/core-shell blends compared to neat PLA and Core-shell blends. All the samples were subjected to TGA analysis, to investigate their thermal stabilities in comparison to their individual polymer components. The individual core and shell polymers start degrading at higher temperatures of 304 °C as shown in Figure 10(a). Thermal stabilities of core shell nanoparticles were found to be comparable and have shown no profound effect of variation in the experimental conditions like #2-3rd_MMA10_30phr. The blends were exhibited a weight loss of about 60 wt% when the temperature is up to 344 °C due to the degradation of the Core-shell on the PLA, as shown in Figure 10(b). The DSC curves of all the samples are shown in Figure 11. The #2-3rd_MMA10_30phr shows a glass transition (T_g) at 66 °C, and #2-3rd_MMA10_30phr show
a glass transition at 63 °C. In this result, the thermal stability of the blend (#2-3rd_MMA10_30phr) show a glass transition was increased by 4 °C compare to neat PLA.

3.6 Mechanical properties of PLA/various impact modifier blends

Tensile properties of neat PLA and PLA/various impact modifier blends are shown in Figure 12. The main tensile properties such as tensile stress are presented in Table 2. The tensile strength and modulus of PLA decreased almost linearly with increasing EM600 content. Tensile strength and modulus decreased by 53.05 and 17.46 %, respectively, by adding 10 phr EM600 in the blends. The lower tensile strength and modulus of EM600 compared to those of neat PLA produced this anticipated result. As the concentration of EM600 increased, it became the dominant component of the blend, and the compounds became softer and flexible, with a lower tensile strength and modulus. The elongation at break (Figure 13 and presented in Table 3) of the blend containing 10 phr of EM600 impact modifier was 390%, indicating a 10 fold increase compared to neat PLA.

The impact strength of neat PLA and PLA/ various impact modifier blends is shown in Figure 14 and presented in Table 4. For each composition, IM812 incorporation increased the notched Izod impact resistance over that of neat PLA (2.05 kgf-cm/cm). The smallest increase was seen with addition of 5 phr IM 812 (3.1±0.09 kgf-cm/cm). The highest impact value for blends in this study was 3.92±0.07 kgf-cm/cm, which was obtained from 10 phr IM812 composition.
It should be noted that the modified PLA maintains quite high tensile modulus and tensile strength with the obviously increased impact strength, which means that the obtained material has a good toughness balance.

3.7 Morphology of fractured surface with commercial impact modifier

Several studies have been reported occurrence of various energy-dissipative mechanisms locally in a stressed specimen before crack development. Mechanisms such as crazing, bond rupture, cavitation, crack growth, plastic and viscoelastic deformations, etc., relieve stresses and consequently reduce the stored elastic energy. High strength and toughness therefore, result primarily from special combination of these mechanisms that retard or limit the growth of cracks. Fractured surfaces of notched Izod impact tested samples showed differentiating brittle to ductile fractures. Hiroi et al., reported noticeable whitening only occurs at the origin of the notched tip for brittle fracture, while ductile fracture involves all of the material around the fractured surface in stress whitening and forms a yielding zone. In rubber-toughened plastic systems, two types of cavitation induced by impact or tensile tests are discerned, which includes internal cavitation in the rubber domains for the blends with strong interfacial adhesion and debonding cavitation between the interfaces with insufficient interfacial adhesion. Generally, the mechanisms which cause damage during brittle fracture have been prescribed as mainly
crazing or microcracks or cavitation. Crazing, cavitation, shear banding, crack bridging and shear yielding reportedly occur as important energy dissipation processes involved in the impact fracture of toughened polymer systems. SEM images of the notched impact fractured surfaces of neat PLA and PLA/commercial impact modifier blends are shown in Figure 15 (a) – 15(f) In the case of core-shell blends are uniformly distributed in the PLA matrix, and their surface is very rough. Moreover, evident cavitation caused by debonding and stress whitening near the notched tip due to crazing/microcracks resulted. Although debonding absorbs a considerable amount of fracture energy.
4. CONCLUSIONS

A series of core–shell latices comprising a core of the rubbery acrylic alkyl ester copolymers and a surrounding shell of glassy PMMA copolymers were designed and synthesized via a semi-continuous seeded emulsion polymerization. Particle size analysis showed that the core-shell morphology was effectively formed in the copolymerization. Emulsion particles were found to be uniform in size by the ELS. By blending of PLA with the BA-MMA core-shell particles, up to 10 fold increase in the impact strength of PLA was achieved. SEM, DSC and Tg analyses indicated that the synthesized polyacrylate emulsion particles had a clear core-shell structure, and they showed good thermal stability. The highest impact performance was obtained by addition of #2-3rd_MMA5. As observed in the SEM images, the fractured surfaces of the blend samples with 5 or more #2-3rd_MMA5 were rough, which is indicative of the improved toughness. The core-shell particles showed a high toughening efficiency for PLA and also fine dispersion characteristics.
5. REFERENCES


Table 1. Recipes for core-shell emulsion polymerization

|     | Core |                      | Shell |                      |                    |                      |                    |
|-----|------|----------------------|-------|----------------------|--------------------|--------------------|
|     | DI water (g) | SLS (g) | KPS (g) | Seed (g) | BA (g) | EGDMA (g) | Particle size (nm) | DI water (g) | KPS (g) | Seed (g) | MMA (g) | Particle size (nm) |
| #1-1<sup>st</sup> | 200 | 0.05 | 0.2 | 0 | 50 | 0 | 149.5 ± 16.7 | 140 | 0.1 | 50 | 10 | 202.3 ± 18.1 |
| #1-2<sup>nd</sup> | 180 | 0.05 | 0.2 | 25 | 45 | 0 | 306.5 ± 34.5 | 140 | 0.1 | 50 | 10 | 353.7 ± 31.3 |
| #1-3<sup>rd</sup> | 180 | 0.05 | 0.2 | 25 | 45 | 0 | 572.3 ± 90.3 | 140 | 0.1 | 50 | 10 | 620.3 ± 95.5 |
| #2-1<sup>st</sup> | 200 | 0.05 | 0.2 | 0 | 47.5 | 2.5 | 189.2 ± 21.5 | 140 | 0.1 | 50 | 10 | 241.1 ± 23.2 |
| #2-2<sup>nd</sup> | 180 | 0.05 | 0.2 | 50 | 42.5 | 2.5 | 442.4 ± 67.7 | 140 | 0.1 | 10 | 505.8 ± 52.4 |
| #2-3<sup>rd</sup> | 180 | 0.05 | 0.2 | 50 | 42.5 | 2.5 | 751.7 ± 102.1 | 140 | 0.1 | 50 | 10 | 825.2 ± 101.4 |
|     |      |                      |       |       |       |       |                   |      |       |       |      |                   |
|     | 140 | 0.1 | 50 | 5 | 779.2 ± 89.2 |
|     | 140 | 0.1 | 50 | 20 | 898.5 ± 88.2 |
### Table 2. Tensile strength (MPa) of neat PLA and PLA/ commercial impact modifiers blend

<table>
<thead>
<tr>
<th>Samples</th>
<th>1 phr</th>
<th>3 phr</th>
<th>5 phr</th>
<th>10 phr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat PLA</td>
<td>64.82</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ABS (10%)</td>
<td>69.92</td>
<td>67.75</td>
<td>67.1</td>
<td>67.87</td>
</tr>
<tr>
<td>ABS (15%)</td>
<td>69.23</td>
<td>69.5</td>
<td>69.31</td>
<td>66.52</td>
</tr>
<tr>
<td>ABS (20%)</td>
<td>69.01</td>
<td>64.75</td>
<td>63.64</td>
<td>61.7</td>
</tr>
<tr>
<td>IM810</td>
<td>61.1</td>
<td>60.56</td>
<td>58.54</td>
<td>55.88</td>
</tr>
<tr>
<td>IM812</td>
<td>61.94</td>
<td>60.46</td>
<td>56.27</td>
<td>54.5</td>
</tr>
<tr>
<td>EM600</td>
<td>63.7</td>
<td>62.39</td>
<td>58.24</td>
<td>53.05</td>
</tr>
</tbody>
</table>
Table 3. Elongation at break (%) of neat PLA and PLA/ commercial impact modifiers blend

<table>
<thead>
<tr>
<th>Samples</th>
<th>1 phr</th>
<th>3 phr</th>
<th>5 phr</th>
<th>10phr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat PLA</td>
<td>14.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ABS (10%)</td>
<td>15.6</td>
<td>15.1</td>
<td>8.6</td>
<td>8.6</td>
</tr>
<tr>
<td>ABS (15%)</td>
<td>12</td>
<td>9</td>
<td>8.5</td>
<td>8.1</td>
</tr>
<tr>
<td>ABS (20%)</td>
<td>12.9</td>
<td>9</td>
<td>15.3</td>
<td>8.3</td>
</tr>
<tr>
<td>IM810</td>
<td>13.3</td>
<td>13.9</td>
<td>11.6</td>
<td>229.8</td>
</tr>
<tr>
<td>IM812</td>
<td>13.3</td>
<td>10.2</td>
<td>10.2</td>
<td>371</td>
</tr>
<tr>
<td>EM600</td>
<td>11.2</td>
<td>327.4</td>
<td>338</td>
<td>390.4</td>
</tr>
</tbody>
</table>
Table 4. Impact strength (kgf-cm/cm) of neat PLA and PLA/commercial impact modifiers blend

<table>
<thead>
<tr>
<th>Samples</th>
<th>1 phr</th>
<th>3 phr</th>
<th>5 phr</th>
<th>10 phr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat PLA</td>
<td>2.05</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ABS (10%)</td>
<td>2.76</td>
<td>2.53</td>
<td>3.22</td>
<td>3.11</td>
</tr>
<tr>
<td>ABS (15%)</td>
<td>2.73</td>
<td>3.11</td>
<td>2.8</td>
<td>3.34</td>
</tr>
<tr>
<td>ABS (20%)</td>
<td>2.42</td>
<td>2.57</td>
<td>3.22</td>
<td>3.26</td>
</tr>
<tr>
<td>IM810</td>
<td>2.38</td>
<td>2.74</td>
<td>3.07</td>
<td>3.43</td>
</tr>
<tr>
<td>IM812</td>
<td>2.92</td>
<td>2.92</td>
<td>3.1</td>
<td>3.92</td>
</tr>
<tr>
<td>EM600</td>
<td>2.82</td>
<td>3.05</td>
<td>2.97</td>
<td>3.17</td>
</tr>
</tbody>
</table>
(A) Reactor  (B) Agitator  (C) Temperature indicator  (D) Temperature controller  (E) Pressure gauge

Figure 1. Schematic diagram of core-shell particle preparation set-up.
Figure 2. Particle size distribution of the final core-shell emulsion particle: (a) before crosslinking with EGDMA, and (b) after crosslinking with EGDMA.
Figure 3. Scheme of the core-shell particle containing polyacrylate emulsion.
Figure 4. SEM images of the core-shell particles (a), (b) without EGDMA and (c) – (f) with EGDMA:
(a) #1-1st_MMA 10, (b) #1-3rd_MMA 10, (c) #2-3rd_MMA 5,
(d) #2-1st_MMA 5, (d) #2-1st_MMA 10, (e) #2-3rd_MMA 10,
(f) #2-3rd_MMA 20.
Figure 5. Impact strength of the PLA/core-shell particle blends (a) – (c) without EGDMA and (d) – (h) with EGDMA:

(■) #1-1<sup>st</sup>_MMA 10, (◧) #1-2<sup>nd</sup>_MMA 10, (◨) #1-3<sup>rd</sup>_MMA 10,
(●) #2-1<sup>st</sup>_MMA 10, (◐) #2-2<sup>nd</sup>_MMA 10, (◑) #2-3<sup>rd</sup>_MMA 10,
(▲) #2-3<sup>rd</sup>_MMA 5, (▼) #2-3<sup>rd</sup>_MMA 20, (□) neat PLA.
Figure 6. Tensile strength of the PLA/core-shell blends (a) – (c) without EGDMA and (d) – (h) with EGDMA:

(■)#1-1\textsuperscript{st}MMA 10, (□) #1-2\textsuperscript{nd}MMA 10, (▲) #1-3\textsuperscript{rd}MMA 10,
(●) #2-1\textsuperscript{st}MMA 10, (○) #2-2\textsuperscript{nd}MMA 10, (◑) #2-3\textsuperscript{rd}MMA 10,
(▲) #2-3\textsuperscript{rd}MMA 5, (▼) #2-3\textsuperscript{rd}MMA 20, (□) neat PLA.
Figure 7. Young’s modulus of the PLA/core-shell blends (a) – (c) without EGDMA and (d) – (h) with EGDMA:

(■) #1-1$^{st}$_MMA 10, (◧) #1-2$^{nd}$_MMA 10, (◨) #1-3$^{rd}$_MMA 10,
(●) #2-1$^{st}$_MMA 10, (◐) #2-2$^{nd}$_MMA 10, (◑) #2-3$^{rd}$_MMA 10,
(▲) #2-3$^{rd}$_MMA 5, (▼) #2-3$^{rd}$_MMA 20, (□) neat PLA.
Figure 8. Elongation at break of the PLA/core-shell blends (a) –(c) without EGDMA and (d) – (h) with EGDMA:

(■) #1-1st_MMA 10, (◧) #1-2nd_MMA 10, (◨) #1-3rd_MMA 10, (●) #2-1st_MMA 10, (◐) #2-2nd_MMA 10, (◑) #2-3rd_MMA 10, (▲) #2-3rd_MMA 5, (▼) #2-3rd_MMA 20, (□) neat PLA.
Figure 9. Morphology of impact fractured surface (various impact modifier):
(a) PLA/ABS(10%) blend, (b) PLA/ABS(15%) blend, (c) PLA/ABS (20%) blend, (d) PLA/IM810 blend, (e) PLA/IM812 blend, (f) PLA/AR-PLA blend.
Figure 10. Thermogravimetric analysis of the PLA/core-shell blends with EGDMA: (a) at different core size, (b) at different content of core-shell particle.
Figure 11. Glass Transition Behavior of PLA/core-shell Blends with EGDMA:
(a) at different core size, (b) at different content of core-shell particle.
Figure 12. Tensile strength of the PLA/various impact modifier blends:

- ( ) ABS10%, ( ) ABS15%, ( ) ABS20%, ( ) IM810, ( ) IM812,
- ( ) EM600.
Figure 13. Elongation at break of the PLA/various impact modifier blends:

- (■) ABS10%, (◧) ABS15%, (◨) ABS20%, (●) IM810, (◐) IM812, (◑) EM600.
Figure 14. Impact strength of the PLA/Various impact modifier blends:

(■) ABS10%, (□) ABS15%, (▲) ABS20%, (●) IM810, (○) IM812, (◑) EM600.
Figure 15. SEM images of Izod-fractured surface of the PLA/core-shell blends:
(a) #2-1st_MMA10_20phr, (b) #2-2nd_MMA10_20phr, (c) #2-3rd_MMA10_20phr, (d) #2-3rd_MMA5_30phr, (e) #2-3rd_MMA10_30phr, (f) #2-3rd_MMA20_30phr.