EFFECTS OF COMPATIBILIZER ON MORPHOLOGY, MECHANICAL AND THERMAL PROPERTIES OF POLYLACTIC ACID/NATURAL RUBBER BLEND

NUR SYAZANA BINTI ABDULLAH SANI

A thesis submitted in fulfillment of the requirements for the award of the degree of Master of Engineering (Polymer)

Faculty of Chemical & Energy Engineering
Universiti Teknologi Malaysia

DECEMBER 2015
“I dedicate this entire work to my beloved parents, sisters and younger brother.. 

Thanks for the love and support”
ACKNOWLEDGEMENT

In the name of Allah, the Most Beneficent and the Most Merciful. All praises to Allah the Almighty for giving me the strengths, guidance and patience in completing this thesis. With His blessing, this thesis is finally accomplished.

First of all I would like to express my genuine gratitude to my supervisor Dr Agus bin Arsad and P.M. Dr. Abdul Razak bin Rahmat for their support and encouragement during period of my studies. Your practical view and guidance on my research work was of the utmost importance. Thank you very much for the unending help throughout the course of my research.

My sincere thanks to my beloved parents, Mr. Hj. Abdullah Sani Bin Ramli and Mrs. Hjh. Marbiah Bte Mohamad for their endless love, prayers and tolerance. To my wonderful sisters and younger brother, thank you for your persevering support and encouragement.

A special appreciation towards all my beloved friends, Shaifful Shazmie, Nor Nisa Balqis, Nurul Husna, Siti Najiah, Nurul Ain, Nur Azmyra, Noora’tiqah, Mohd Shaiful Zaidi and Muhamad Rasyidi for giving their everlasting support towards me through thick or thin and being there for me when I needed them the most. Not forgetting to thank the staff of Polymer Engineering Department of Faculty of Chemical Engineering especially Mr Izat, Mr Suhee and Miss Zainab for helping me throughout the research. Without those helps, there would be no possibility for this thesis to be completed. Thank you.
ABSTRACT

The primary focus of this study was to prepare two types of compatibilizers, i.e. polylactic acid-grafted-maleic anhydride (PLA-g-MA) and natural rubber-grafted-maleic anhydride (NR-g-MA) for PLA/NR blends. In the first phase of the study, PLA/NR blends with different NR concentration in the range of 5 to 20 wt% were fabricated. Experimental results showed that PLA/NR blend containing 5 wt% of NR concentration (designated as PLA95/NR5) was the optimum blend due to its higher impact strength (35.74 J/m) and elongation at break (1.84%) as compared to other PLA/NR blends. In the second phase of the study, the two types of compatibilizers (PLA-g-MA and NR-g-MA) with different MA concentrations in the range of 3 to 12 phr were prepared using melt grafting free-radical polymerization method. It was found that the optimum MA concentration for grafting PLA and NR were both 9 phr with the degree of grafting of 1.63% and 5.02%, respectively. In the third phase, the PLA95/NR5 blend was incorporated with different compatibilizers (PLA-g-MA and NR-g-MA) at various loadings (1-10 phr). The experimental results of the mechanical properties, i.e. impact strength, elongation at break and storage modulus of the PLA95/NR5 blend did not show significant enhancement upon addition of PLA-g-MA in the blend. Scanning electron microscope results showed better interfacial adhesion between PLA and NR phases upon addition of 3 phr PLA-g-MA into the blend. The improvement in the interfacial adhesion of the blend could be attributed to the good dispersion of the NR particles in the PLA matrix with the aid of PLA-g-MA compatibilizer. On the contrary, the addition of NR-g-MA did not show much improvement in the mechanical properties of the PLA95/NR5 blend but thermal stability of the blend was increased as compared to the PLA95/NR5. In all tests, further increased of PLA-g-MA and NR-g-MA up to 5 phr and 10 phr, respectively in the PLA95/NR5 blend caused the blend stiffness to increase. This possibly due to an increase in the amount of MA and the reduction of NR elasticity.
ABSTRAK

Fokus utama kajian ini adalah untuk menyediakan dua jenis penserasi, iaitu asid polilaktik-cantuman-maleik anhidrida (PLA-g-MA) dan getah asli-cantuman-maleik anhidrida (NR-g-MA) untuk campuran PLA/NR. Pada fasa pertama kajian ini, campuran PLA/NR dengan kepekatan NR yang berbeza-beza dalam julat antara 5 hingga 20% berat telah direka. Hasil kajian mendapati bahawa campuran PLA/NR dengan kepekatan NR sebanyak 5% berat (ditetapkan sebagai PLA95/NR5) adalah gabungan optimum kerana mempunyai kekuatan hentaman (35.74 J/m) dan pemanjangan pada takat putus (1.84%) yang lebih tinggi berbanding campuran PLA/NR yang lain. Pada fasa kedua kajian, dua jenis penserasi (PLA-g-MA dan NR-g-MA) dengan kepekatan MA yang berbeza-beza dalam julat antara 3 hingga 12 phr telah disediakan menggunakan kaedah pempolimeran cantuman leburan radikal lebas. Keputusan kajian mendapati bahawa kepekatan optimum MA bagi cantuman PLA dan NR adalah masing-masing sebanyak 9 phr dengan darjah cantuman adalah 1.63% dan 5.02%. Pada fasa ketiga kajian, campuran PLA95/NR5 telah digabungkan dengan penserasi (PLA-g-MA dan NR-g-MA) dengan muatan yang berbeza-beza (1-10 phr). Keputusan eksperimen sifat-sifat mekanik, iaitu kekuatan hentaman, pemanjangan pada takat putus dan modulus penyimpanan campuran PLA95/NR5 tidak menunjukkan peningkatan yang ketara dengan penambahan PLA-g-MA di dalam campuran tersebut. Hasil pengimbasan mikroskop elektron menunjukkan bahawa lekatan antara muka di antara fasa PLA dan NR menjadi lebih baik dengan penambahan 3 phr PLA-g-MA ke dalam campuran tersebut. Peningkatan pada lekatan antara muka campuran tersebut boleh dikaikatkan dengan penyebaran partikel NR yang baik dalam matriks PLA dengan bantuan penserasi PLA-g-MA. Sebaliknya, penambahan NR-g-MA tidak menunjukkan banyak peningkatan pada sifat mekanikal campuran PLA95/NR5 tetapi kestabilan haba campuran telah meningkat berbanding dengan PLA-g-MA. Dalam kesemua ujian, penambahan PLA-g-MA dan NR-g-MA masing-masing sehingga 5 phr dan 10 phr ke dalam campuran PLA95/NR5 menyebabkan kekakuan campuran akan meningkat. Ini mungkin disebabkan oleh peningkatan jumlah MA dan pengurangan keanjalan NR.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>CHAPTER</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>DECLARATION</td>
<td>ii</td>
<td></td>
</tr>
<tr>
<td>DEDICATION</td>
<td>iii</td>
<td></td>
</tr>
<tr>
<td>ACKNOWLEDGEMENT</td>
<td>iv</td>
<td></td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>v</td>
<td></td>
</tr>
<tr>
<td>ABSTRAK</td>
<td>vi</td>
<td></td>
</tr>
<tr>
<td>TABLE OF CONTENTS</td>
<td>vii</td>
<td></td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>xi</td>
<td></td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>xii</td>
<td></td>
</tr>
<tr>
<td>LIST OF ABBREVIATION</td>
<td>xv</td>
<td></td>
</tr>
<tr>
<td>LIST OF SYMBOLS</td>
<td>xvii</td>
<td></td>
</tr>
</tbody>
</table>

1 INTRODUCTION  1
1.1 Background of Study  1
1.2 Problem Statement  3
1.3 Objectives of Research  4
1.4 Scope of Research  4

2 LITERATURE REVIEW  6
2.1 Polylactic Acid (PLA)  6
  2.1.1 Properties of PLA  8
  2.1.2 PLA Blends  10
2.2 Natural Rubber (NR)  13
  2.2.1 NR Blends  14
2.3 PLA/NR Blends  16
2.4 Synthesis of Compatibilizer
  2.4.1 Monomer - Maleic Anhydride (MA)
2.5 PLA/MA Blends
2.6 NR/MA Blends

3. METHODOLOGY
  3.1 Materials
    3.1.1 Polylactic Acid (PLA)
    3.1.2 Natural Rubber (NR)
    3.1.3 Monomer
    3.1.4 Initiator
  3.2 Preparation of Compatibilizers
    3.2.1 PLA-g-MA Compatibilizer
    3.2.2 NR-g-MA Compatibilizer
    3.2.3 Characterization of Compatibilizers
      3.2.3.1 Direct Titration Method
      3.2.3.2 Fourier Transform Infrared Spectroscopy (FTIR)
      3.2.3.3 Proton Nuclear Magnetic Resonance (1H-NMR)
  3.3 Polymer Blends Preparation
  3.4 Characterization of PLA/NR and PLA/NR/Compatibilizer
    3.4.1 Mechanical Testing
      3.4.1.1 Tensile Test
      3.4.1.2 Flexural Test
      3.4.1.3 Izod Impact Test
    3.4.2 Differential Scanning Calorimetry (DSC)
    3.4.3 Thermogravimetric Analysis (TGA)
    3.4.4 Fourier Transform Infrared Spectroscopy (FTIR)
    3.4.5 Scanning Electron Microscope (SEM)
    3.4.6 Dynamic Mechanical Analysis (DMA)
RESULTS AND DISCUSSION

4.1 Properties of PLA/NR Blends

4.1.1 Mechanical Properties

4.1.1.1 Izod Impact Test

4.1.1.2 Tensile Strength

4.1.1.3 Young’s Modulus

4.1.1.4 Elongation at Break

4.1.1.5 Flexural Strength and Modulus

4.1.2 Thermal Properties

4.1.2.1 Thermogravimetric Analysis (TGA)

4.1.2.2 Differential Scanning Calorimetry (DSC)

4.1.3 Morphology

4.1.3.1 Scanning Electron Microscope (SEM)

4.2 Analysis of Compatibilizer PLA-g-MA and NR-g-MA

4.2.1 PLA-g-MA Compatibilizer

4.2.2 NR-g-MA Compatibilizer

4.3 Compatibilized PLA/NR Blends

4.3.1 Mechanical Properties

4.3.1.1 Tensile Properties

4.3.1.2 Elongation at Break

4.3.1.3 Flexural Properties

4.3.1.4 Izod Impact Test

4.3.2 Thermal Properties

4.3.2.1 Thermogravimetric Analysis (TGA)

4.3.2.2 Differential Scanning Calorimetry (DSC)

4.3.3 Fourier Transform Infrared Spectroscopy (FTIR)

4.3.4 Morphological Study

4.3.5 Dynamic Mechanical Analysis (DMA)
5 CONCLUSION AND RECOMMENDATIONS 84
5.1 Conclusion 84
5.2 Recommendation 85

REFERENCES 87

Appendices 98-99
<table>
<thead>
<tr>
<th>TABLE NO.</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Properties of PLA, PS and PET</td>
<td>9</td>
</tr>
<tr>
<td>3.1</td>
<td>Typical properties for PLA 1323A</td>
<td>27</td>
</tr>
<tr>
<td>3.2</td>
<td>Grafting composition of PLA-g-MA</td>
<td>29</td>
</tr>
<tr>
<td>3.3</td>
<td>Grafting composition of NR-g-MA</td>
<td>30</td>
</tr>
<tr>
<td>3.4</td>
<td>Formulation for PLA/NR blends</td>
<td>33</td>
</tr>
<tr>
<td>3.5</td>
<td>Formulation for PLA/NR compatibilized blends</td>
<td>33</td>
</tr>
<tr>
<td>4.1</td>
<td>TGA results of PLA and PLA/NR blends</td>
<td>48</td>
</tr>
<tr>
<td>4.2</td>
<td>Thermal characteristics of PLA and PLA/NR blends</td>
<td>50</td>
</tr>
<tr>
<td>4.3</td>
<td>TGA results of PLA/NR/PLA-g-MA blends</td>
<td>70</td>
</tr>
<tr>
<td>4.4</td>
<td>TGA results of PLA/NR/NR-g-MA blends</td>
<td>70</td>
</tr>
<tr>
<td>4.5</td>
<td>Thermal characteristics of PLA/NR/PLA-g-MA blends</td>
<td>72</td>
</tr>
<tr>
<td>4.6</td>
<td>Thermal characteristics of PLA/NR/NR-g-MA blends</td>
<td>73</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>FIGURE NO.</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Chemical structure of L and D-lactic acid</td>
<td>6</td>
</tr>
<tr>
<td>2.2</td>
<td>Synthesis methods for high molecular weight PLA</td>
<td>7</td>
</tr>
<tr>
<td>2.3</td>
<td>Straight chain polymer structure of cis and trans-1,4 polyisoprene</td>
<td>13</td>
</tr>
<tr>
<td>2.4</td>
<td>SEM micrographs of fractured surfaces of the blends (a) 10% NR, (b) 10% NR-g-PMMA (c) 10% ENR25</td>
<td>17</td>
</tr>
<tr>
<td>2.5</td>
<td>Compatibilization in polymer blends</td>
<td>19</td>
</tr>
<tr>
<td>2.6</td>
<td>Molecular structure of MA</td>
<td>21</td>
</tr>
<tr>
<td>2.7</td>
<td>Mechanism of maleated PLA</td>
<td>22</td>
</tr>
<tr>
<td>2.8</td>
<td>Mechanism of maleated natural rubber (NR-g-MA)</td>
<td>25</td>
</tr>
<tr>
<td>4.1</td>
<td>Impact strength with different percentage of NR</td>
<td>39</td>
</tr>
<tr>
<td>4.2</td>
<td>Tensile strength with different percentage of NR</td>
<td>41</td>
</tr>
<tr>
<td>4.3</td>
<td>Young’s modulus with different percentage of NR</td>
<td>42</td>
</tr>
<tr>
<td>4.4</td>
<td>Elongation at break with different percentage of NR</td>
<td>43</td>
</tr>
<tr>
<td>4.5</td>
<td>Flexural strength with different percentage of NR</td>
<td>44</td>
</tr>
<tr>
<td>4.6</td>
<td>Flexural modulus with different percentage of NR</td>
<td>45</td>
</tr>
<tr>
<td>4.7</td>
<td>TGA curves of PLA and PLA/NR blends with different percentage of NR</td>
<td>47</td>
</tr>
<tr>
<td>4.8</td>
<td>DTG curves of PLA and PLA/NR blends with different percentage of NR</td>
<td>47</td>
</tr>
</tbody>
</table>
4.9 DSC thermograms of PLA and PLA/NR blends with different percentage of NR 

4.10 SEM micrographs of PLA/NR blends: (a) pure PLA, (b) PLA95/NR5, (c) PLA90/NR10, (d) PLA85/NR15 and (e) PLA80/NR20 

4.11 The degree of grafting of grafted PLA. 

4.12 FTIR spectra of (a) MA and (b) PLA and PLA-g-MA with highest degree of grafting (9 phr) 

4.13 $^1$H-NMR spectra of (a) PLA pure and (b) grafted PLA 

4.14 The degree of grafting of grafted NR 

4.15 FTIR spectra of NR and NR-g-MA with the highest degree of grafting (9 phr) 

4.16 $^1$H-NMR spectra of (a) NR pure and (b) grafted NR 

4.17 Tensile strength of PLA/NR blends at various contents of compatibilizer 

4.18 Young’s modulus of PLA/NR blends at various contents of compatibilizer 

4.19 Elongation at break of PLA/NR blends at various contents of compatibilizer 

4.20 Flexural strength of PLA/NR blends at various contents of compatibilizer 

4.21 Flexural modulus of PLA/NR blends at various contents of compatibilizer 

4.22 Impact strength of PLA/NR blends at various contents of compatibilizer 

4.23 TGA curves of PLA/NR blends at various contents of PLA-g-MA 

4.24 TGA curves of PLA/NR blends at various contents of NR-g-MA 

4.25 DSC thermograms of PLA/NR blends at various contents of PLA-g-MA 

4.26 DSC thermograms of PLA/NR blends at various contents of NR-g-MA
4.27 FTIR spectra of PLA/NR blend and compatibilized PLA/NR  

4.28 Schematic reaction in the blends between PLA-g-MA and NR  

4.29 Schematic reaction in the blends between NR-g-MA and PLA  

4.30 SEM micrographs of PLA/NR/PLA-g-MA blends: (a) PLA/NR, (b) 3 phr PLA-g-MA, (c) 10 phr PLA-g-MA, (d) 3 phr PLA-g-MA and (e) 10 phr PLA-g-MA  

4.31 The storage modulus vs. Temperature obtained from DMA of PLA/NR and the blends: a) PLA-g-MA b) NR-g-MA  

4.32 The loss modulus vs. Temperature obtained from DMA of PLA/NR and the blends: a) PLA-g-MA b) NR-g-MA  

4.33 The tan δ vs. Temperature obtained from DMA of PLA/NR and the blends: a) PLA-g-MA b) NR-g-MA.
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AEM</td>
<td>Ethylene-acrylic rubber</td>
</tr>
<tr>
<td>BPO</td>
<td>Benzoyl peroxide</td>
</tr>
<tr>
<td>DMA</td>
<td>Dynamic Mechanical Analysis</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>DTG</td>
<td>Derivative Thermogravimetric</td>
</tr>
<tr>
<td>EGMA</td>
<td>Poly(ethylene-glycidyl methacrylate)</td>
</tr>
<tr>
<td>ENR</td>
<td>Epoxidized natural rubber</td>
</tr>
<tr>
<td>EPM</td>
<td>Ethylene-propylene copolymer</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared Spectroscopy</td>
</tr>
<tr>
<td>GMA</td>
<td>Glycidyl methacrylate</td>
</tr>
<tr>
<td>HBP</td>
<td>Hyperbranched poly(ester amide)</td>
</tr>
<tr>
<td>HDPE</td>
<td>High density polyethylene</td>
</tr>
<tr>
<td>\textsuperscript{1}H-NMR</td>
<td>Proton Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>IR</td>
<td>Isoprene rubber</td>
</tr>
<tr>
<td>LGM</td>
<td>Lembaga Getah Malaysia</td>
</tr>
<tr>
<td>MA</td>
<td>Maleic anhydride</td>
</tr>
<tr>
<td>MAPLA</td>
<td>Maleated polylactide</td>
</tr>
<tr>
<td>NBR</td>
<td>Nitrile-butadiene rubber</td>
</tr>
<tr>
<td>NR</td>
<td>Natural rubber</td>
</tr>
<tr>
<td>NR-g-MA</td>
<td>Natural rubber-grafted-maleic anhydride</td>
</tr>
<tr>
<td>PCL</td>
<td>Polycaprolactone</td>
</tr>
<tr>
<td>PE</td>
<td>Polyethylene</td>
</tr>
<tr>
<td>PET</td>
<td>Poly(ethylene terephthalate)</td>
</tr>
<tr>
<td>phr</td>
<td>Part per hundred resin</td>
</tr>
<tr>
<td>Acronym</td>
<td>Full Form</td>
</tr>
<tr>
<td>---------</td>
<td>-----------</td>
</tr>
<tr>
<td>PLA</td>
<td>Polylactic acid</td>
</tr>
<tr>
<td>PLA-g-MA</td>
<td>Polylactic acid-grafted-maleic anhydride</td>
</tr>
<tr>
<td>PMMA</td>
<td>Poly(methyl methacrylate)</td>
</tr>
<tr>
<td>PP</td>
<td>Polypropylene</td>
</tr>
<tr>
<td>PS</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>PVAc</td>
<td>Poly(Vinyl Acetate)</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>SNR</td>
<td>Styrene-based deproteinized natural rubber</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric Analysis</td>
</tr>
<tr>
<td>TPEE</td>
<td>Thermoplastic polyester elastomer</td>
</tr>
<tr>
<td>TPS</td>
<td>Thermoplastic starch</td>
</tr>
<tr>
<td>TPU</td>
<td>Thermoplastic polyurethane</td>
</tr>
<tr>
<td>ULDPE</td>
<td>Ultra low density polyethylene</td>
</tr>
</tbody>
</table>
**LIST OF SYMBOLS**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E'$</td>
<td>Storage modulus</td>
</tr>
<tr>
<td>$E''$</td>
<td>Loss modulus</td>
</tr>
<tr>
<td>g/cm³</td>
<td>gram per centimeter cube</td>
</tr>
<tr>
<td>GPa</td>
<td>Giga Pascal</td>
</tr>
<tr>
<td>J/m</td>
<td>Joule per meter</td>
</tr>
<tr>
<td>kJ/m²</td>
<td>kiloJoule per meter square</td>
</tr>
<tr>
<td>ml</td>
<td>milliliter</td>
</tr>
<tr>
<td>MPa</td>
<td>Mega Pascal</td>
</tr>
<tr>
<td>rpm</td>
<td>revolution per minute</td>
</tr>
<tr>
<td>$\tan \delta$</td>
<td>Tangent delta</td>
</tr>
<tr>
<td>$T_{cc}$</td>
<td>Cold crystallization temperature</td>
</tr>
<tr>
<td>$T_g$</td>
<td>Glass transition temperature</td>
</tr>
<tr>
<td>$T_m$</td>
<td>Melting temperature</td>
</tr>
<tr>
<td>$T_{max}$</td>
<td>Maximum temperature</td>
</tr>
<tr>
<td>$T_{onset}$</td>
<td>Onset temperature</td>
</tr>
<tr>
<td>w/w</td>
<td>Weight per weight</td>
</tr>
<tr>
<td>wt%</td>
<td>Weight percentage</td>
</tr>
<tr>
<td>$X_c$</td>
<td>Degree of crystallinity</td>
</tr>
<tr>
<td>$\Delta H_f$</td>
<td>Heat of fusion</td>
</tr>
<tr>
<td>µm</td>
<td>Micrometer</td>
</tr>
</tbody>
</table>
CHAPTER 1

INTRODUCTION

1.1 Background of Study

Plastic materials produced from petrochemicals has became a great used in packaging, automotive, healthcare application, and communication or electronic industries. As these conventional synthetic polymers are not easily degraded because of their high molecular mass and hydrophobic character, may accumulate in the environment and represent a significant source of environmental pollution potentially harming wildlife. One of the possible solutions to this problem is to replace the petroleum-based plastic with the biodegradable polymers with suitable mechanical and physical properties which have received particular attention. A necessary prerequisite for extending their utilization is their biodegradability in natural environments, which may serve as a source of carbon and energy for a variety of microorganisms.

Polylactic acid (PLA) is known as a biodegradable thermoplastic polymer with wide range of potential application such as disposable packaging, medical implants, textiles and automobile industries (Phruksaphithak and Noomhorm, 2012). The PLA has attracted industrial community’s attention because its starting material, lactic acid, is obtained by a fermentation process from 100% renewable resources. Conventional methods to process PLA are extrusion, injection moulding, blow moulding and thermoforming. The PLA is available in a form of rigid or flexible and have advantages in terms of eco-friendly, biocompatibility, processibility and energy
savings. However, there are some drawbacks of PLA such as too stiff and brittle for room temperature applications, slow degradation rate, hydrophobic nature and lack of reaction side-chain groups (chemically inert) have become major obstacles for expanding its applications as a common plastic material (Rasal et al., 2010). Several strategies have been attempted to overcome these problems, for instance improving mechanical properties by chemical modification through copolymerization and surface modification (Xiao et al., 2012). However, both of these approaches show some limitation in mechanical properties of PLA. The chemical modification in large scale requires expensive equipment and increase in brittleness still remains a problem to be solved. Meanwhile, the surface modification was only focused on biomedical applications of PLA.

Another practical strategy to overcome these drawbacks is by combining PLA with other polymers to create a polymer material with different physical properties (Thomas et al., 2015). This method, so-called polymer blending, has utilized various of synthetic polymers as a second polymer. These include poly(ethylene) (Anderson et al., 2003), polycaprolactone (Wu et al., 2008), poly(butylene succinate) (Yokohara and Yamaguchi, 2008) and poly(vinyl acetate) (Gajria et al., 1999). In general, these blends showed considerably higher toughness than pure PLA. However, these polymers are petroleum based and need to be replaced with biodegradable polymer to minimize negative impact to environment. Therefore, new material from renewable resource such as natural rubber (NR) has attracted much attention as possible second phase polymer, mainly due to its renewability and recovery properties. NR is known to have high molecular weight and very low glass transition temperature about -70°C compared to other synthetic polymer materials. Its excellent properties in terms of mechanical strength, resilience, elongation at break and low cost make NR a remarkable polymer as PLA toughening agent (Wongsorat et al., 2010).

The polymer blend represents a very important field in polymeric materials, which offers better properties in comparison with the neat polymers. It has been reported that the final properties of the polymer blends are related to the quality of their morphology, which in turns depends on a rheological properties of components
of the blend, composition of the blend, processing conditions used to obtain the blend, and the compatibility between the polymers forming the blend (Thomas et al., 2015). Among them, the most important controlling parameter in polymer blend processes is degree of compatibility of the blended polymers (Nawaz et al., 2010). However, literature reveals that most polymer blends are incompatible, resulting in materials with coarse morphology, weak adhesion among phases and poor mechanical properties. The compatibility between the polymers of a blend can be improved by the addition of compatibilizers which results in a finer and more stable morphology, better adhesion between the polymers of the blend and consequently better properties of the final product.

1.2 Problem Statement

The major drawbacks of PLA are its low elongation at break, impact strength, heat deflection temperature and low melt strength. One way to overcome the brittleness of PLA is through polymer blending. In this research work, NR was selected as second polymer phase for PLA. According to Bitinis et al. (2011), the ductility of PLA can be improved by blending with NR due to its high specific strength and modulus, low density, renewability and high elongation at break. However, the difference in the polarity and molecular weight of PLA and NR may also result in poor compatibility and led to poor mechanical properties of the blend. Thus, the compatibility between PLA and NR need to be improved. In this study, a third component called compatibilizer was prepared and used to increase the interaction between the PLA and NR. Two types of compatibilizers were prepared and used which were NR-g-MA and PLA-g-MA. These two compatibilizers were synthesized by melt grafting free-radical polymerization method using maleic anhydride (MA) as a monomer. MA was grafted onto PLA and NR during melt mixing in the presence of benzoyl peroxide (BPO) as an initiator using an internal mixer.
MA was selected in this study due to its good chemical reactivity, low toxicity and low potential to polymerize itself under free radical grafting conditions. In addition, MA was considered for the present study based on the extensive use of grafting MA or maleic copolymers as a compatibilizer in binary immiscible polymer blends as reported by Carone et al. (2000), Zhang and Sun (2004) and Teamsinsungyon et al. (2012). Hence, it is expected that the incorporation of compatibilizers into PLA/NR blend could enhance the interaction between these two polymers as well as mechanical properties of the blend.

1.3 Objectives of Research

The objectives of this study are:

i. To study the influence of NR concentration on the mechanical, thermal and morphology properties of PLA/NR blends.

ii. To synthesize and characterize PLA-g-MA and NR-g-MA compatibilizers.

iii. To investigate the influence of compatibilizers loading on the mechanical, thermal and morphology properties of PLA/NR blends.

1.4 Scope of Research

In order to achieve the objectives of the research, following scopes of work have been performed:

(i) Preparation of PLA/NR blends using four different concentrations of NR ranging from 5 to 20 wt% via melt blending method using a twin screw extruder. Then, the blends were moulded using hot press moulding.
(ii) Investigation on the effect of NR concentration on the morphology, mechanical and thermal properties of the PLA/NR blend and identification of the ideal NR concentration for preparing PLA/NR blend.

(iii) Synthesis of NR-g-MA and PLA-g-MA compatibilizers using melt grafting free-radical polymerization and MA as a monomer.

(iv) Characterization of the compatibilizers using direct titration method, Fourier transform infrared spectroscopy (FTIR) and proton nuclear magnetic resonance (¹H-NMR) in order to determine the degree of grafting and to confirm the existence of MA on PLA structure.

(v) Preparation of polymer blends by using different concentrations of compatibilizer (1 to 10 phr) in the PLA containing 5 wt% NR blend and determination of its mechanical properties using tensile test, flexural test and Izod impact test.

(vi) Characterization of the polymer blend structure and morphology using Fourier transform infrared spectroscopy (FTIR) and scanning electron microscope (SEM), respectively.

(vii) Determination of the thermal degradation behaviour using thermogravimetric analysis (TGA), investigation of the thermal and dynamic mechanical properties of the blends using differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA), respectively.

(viii) Identification of the optimum amount of compatibilizer for PLA/NR blend based on their morphology, mechanical and thermal properties.
REFERENCES


