CHAPTER I
INTRODUCTION

Nowadays, a growing demand for biodegradable polymers is evident. One of the major causes is the world-wide energy crisis. Also, the environmental concerns have brought the need for a more easily degradable material, hence, biopolymers (polymer derived from natural resources) are becoming more important. Polylactide (PLA) is one of the biopolymers that can be obtained from renewable resources such as corn starch or sugarcanes. Natural proteins including gelatin, keratin, collagen, fibroin, and sericin also belong to the biopolymer group. These polymers have potential to be used as a substitute for petroleum based polymer, for example in medical and dental applications.

PLA, a hydrolysable aliphatic polyester with good mechanical properties and biodegradability, can be prepared by two methods. Both approachs use lactic acid as the starting monomer. First method can be achieved through polycondensation of lactic acid resulting in a lower molecular weight of PLA. Another way is through the ring opening polymerization of lactide, the cyclic monomer of lactic acid. However, PLA needs modification for most practical applications due to its stiffness and brittleness. Introducing a low T_g polymer into the polymer backbone can impart the flexibility to PLA. For example, a copolymer can be obtained from the graft copolymerization process.

In 2007, Patcharakamon *et al* synthesized graft copolymer of EVOH-g-PLA by single-step catalytic reactive extrusion. Their technique involves free radical polymerization of a monomer in the presence of EVOH, through a catalytically initiated ring-polymerization procedure of lactide. A catalytic system provides a faster and more effective ring opening polymerization while graft copolymerization can be occurred at the same time. This method is also economically effective. The new technology is important for biodegradable plastic industries in Thailand since agricultural products are abundant and can be fertilized to yeild lactic acid—a precursor of lactide monomers. During reactive extrusion process, monomer can be convertd into polymers and simultaneously shaped to fit the desired applications.

Such processing method, along with a large supply of lactic acid, may lead to a reduction in the need for importing PLA of Thailand.

The success of previous researches leads to the idea of combining PLA with other biodegradable polymers, produced in Thailand to obtain medical products. This work emphasizes on the development of the biocomposite soft splint from polylactide, silk sericin, marl and the adjustment of product strength by introducing benzoxazine structure to a graft copolymer. Polybenzoxazine (PBZ) is a novel class of thermosetting polymer with superior physical properties of traditional polymers, including low water uptake, near-zero shrinkage, and high thermal stability.

Generally, splint is made from fiberglass and plaster, which cause some problems regarding the flexibility and the side effect generated on the inner-splint skin. If these materials become wet, serious problems may occur. When a plaster cast gets wet, the cast becomes soft, loses strength, and may no longer adequately immobilize the injured area. Hence, the broken bones may heal in the incorrect position. When the cotton or synthetic padding gets wet, it is very difficult to dry. As a result, the wet skin under the wet padding may develop rashes, infections, or become macerated. To solve the problems mentioned, protein in silk known as sericin is one of the selected additives to be added into the splint. Because sericin has special properties including anti-bacteria, anti-fungi, and moisture absorption, it can reduce humidity caused from sweat in the splint and be healthful for protecting skin from inflammation and rash. The next filler is marl or marly limestone, or known in Thai as "din-so-pong" which is a traditional herb. Marl is the white soil contained more than 80% calcium carbonate which has several benefits in Thai medical treatment as a cool powder to be used as an anti-sweat, an anti-infection, and skin disease reduction.

All mentioned above lead to the purpose of this research; the preparation of sericin-g-polylactide via in-situ catalytic ring opening polymerization using a brabender mixer. The obtained copolymer will be blended with benzoxazine precursor at mild temperature and filled with marl. The resulting composite will be suituble for a soft splint application. The main processing parameters will be optimized. The mechanical properties and thermal properties will also be investigated.

OBJECTIVES

1. To synthesize benzoxazine precursor and study the effect of marl contents on the properties of polybenzoxazine–marl immiscible composite.
2. To modify surface of a marl filler with (3-aminopropyl) trimethoxy-silane and stearic acid and study the effect of surface modification on the morphology and mechanical properties of polybenzoxazine–marl composite.
3. To synthesize silk sericin-graft-polylactide copolymer with stannous octoate as a catalyst by using a brabender mixer.
4. To investigate the proper ratio of graft copolymer filled with the modified surface marl and benzoxazine precursor on the mechanical and physical properties of the biocomposite.

SCOPE OF RESEARCH

The scope of this research will cover the following:

1. The systhesis of a benzoxazine precursor by using bisphenol-A, aliphatic diamine, and paraformaldehyde via a quasi-solvent approach.
2. The preparation of crude sericin-g-PLA by using in-situ catalytic ring opening polymerization in a brabender mixer.
3. The characterization of a graft copolymer and a polybenzoxazine precursor.
4. The investigation of the effects of marl and modified surface marl filler on the thermal and mechanical properties of polybenzoxazine–marl composite.
5. The fabrication of polybenzoxazine–marl composite and the biocomposite by using a compression moulding process.
6. The thermal and mechanical properties of the biocomposites and their performances are investigated.