CHAPTER I
INTRODUCTION

Ethylene is known as a plant hormone that triggers the ripening of fruit and effects on the growth, development and storage life of many fruits, vegetables and ornamental crops. The control of ethylene in stored environments plays a key role in prolonging the postharvest life of many fresh products. Nowadays, researchers attempt to develop novel and more effective ethylene scavenging materials (for example, as a modified porous clay heterostructures) because of its high surface area with uniform and specific pore sizes. Likely, attractive feature of silk protein derived from silk worm has the interesting efficiency in cross-linking, copolymerizing, and blending with other macromolecular materials, especially artificial polymers to be useful for forming articles.

Among commercially available polymer, poly(lactic acid) (PLA) has gained considerable research interest. PLA not only posses high strength and modulus and biodegradability but also has biocompatibility and yielding nontoxic byproduct after degradation. However, PLA major drawbacks are inherent brittleness and low toughness. Blends of PLA with several synthetic and biopolymers are an effort to enhance the properties of PLA. In 2009, Mahajaroensiri *et al.* studied hardening of silk sericin-g-PLA/MARL biocomposites by polybenzoxazine. They proposed that the graft copolymer from biodegradable PLA was developed to reduce PLA brittleness and cost, and the mechanical properties of the biocomposite hardened were improved. Natural silk is composed of two major proteins named fibroin and sericin. Fibroin is the core protein hold together by the glue like protein called "sericin". In the silk manufacturing, sericin must be removed from the raw silk by "degumming process" and discarded in processing wasted water lead to environmental contamination. It is estimated that 400,000 tons of dry cocoons in the worldwide production, around 50,000 tons of sericin could be recovered (Zhang, 2002). If sericin in silk waste water could recover, it could be significant in terms of economy and environmental benefits. Sericin is useful in many applications range from the cosmetics to improve functional properties of some synthetic fibers. Many researchers find that sericin molecule can be cross-linked such as Yamada and

Matsunaga., 1994 and Yamada *et al.*, 1993 reported a sericin-modified polyester fiber obtained by cross-linking with glyceryl polyglycidyl ether and diethylene triamine to improve hygroscopicity.

Several years ago, the layered silicate also known as clays such as sodium montmorillonite, bentonite, and laponite are extensively used to develop polymer/clay nanocomposites due to their properties such as high surface area, high aspect ratio, and relatively low cost. Interestingly, when layered silicate clays are passed through the environmental friendly process called freeze-drying, it can be rearranged to a new porous structure called the aerogel. The porous structure of the aerogel makes it suitable for using as the ethylene scavenger. Some researchers were interested in prepared porous clay heterostructures (PCHs) into an entrapping system. In 2011, Srithammaraj *et al.* modified porous clay heterostructures by organic-inorganic hybrids for nanocomposite ethylene scavenging/sensor packaging film. They proposed that PCHs showed higher efficiency in absorbing ethylene gas than did bentonite.

Since the properties of sericin, PLA and clay aerogel are appropriated for hygroscopicities, high strength and modulus products, and entrapping systems, respectively. There is possibility to cooperate sericin, PLA and clay aerogel for packaging application such as ethylene scavenging by use plasma treatment and acrylic acid (AAc) to provide cross-linking. A few researchers have been studied the ability of graft co-polymerization AAc onto polymer surface by dielectric barrier discharge (DBD) in air. They proposed that the reactions of graft co-polymerization and homopolymerization compete with each other in the process of graft (Ren, 2006).

In this study, the sericin-g-PLA clay aerogel with acrylic acid is prepared by freeze-drying process. Sericin is extracted from different species of Thai silk cocoon; Nang Noi, Nang Lai, Dok Bua and Luang Pirote and freeze-dried to obtain sericin powder. The sericin-g-PLA clay aerogel with acrylic acid is prepared by varying sericin, clay and acrylic acid contents. After that, the aerogel is treated with air plasma by varying plasma treatment times and the effect of those contents on properties of the aerogel is studied. The aerogel is also studied for morphology, mechanical and thermal properties. Moreover, the aerogel is studied on the possibility to use as ethylene scavengers for the packaging application.

OBJECTIVES

1. To extract sericin from different species of Thai silk cocoons and prepare the sericin-g-PLA to study the effect of Thai silk cocoon species on the solubility, %grafting, molecular weight and chemical structure of the sericin-g-PLA.
2. To prepare the sericin-g-PLA from the cocoon species that gives the highest %grafting and solubility and study the mass ratio of sericin and LA monomer on the solubility, %grafting, molecular weight and chemical structure of the sericin-g-PLA.
3. To prepare the sericin-g-PLA clay aerogel with acrylic acid by freeze-drying process and investigate plasma assisted crosslinking sericin-g-PLA clay aerogel with acrylic acid.
4. To study the effect of clay and acrylic acid contents, sericin and LA monomer ratio and plasma treatment times on the morphology, mechanical and thermal properties of aerogels.
5. To study the possibility to use sericin-g-PLA clay aerogel with acrylic acid as ethylene scavengers for the packaging application.

SCOPE OF RESEARCH

The scope of this research will cover following:

1. The species of Thai silk cocoon; Nang Noi (NN), Nang Lai (NL), Dok Bua (DB) and Luang Pilote (LP) on properties of the sericin-g-PLA such as the solubility, %grafting by using soxhlet, molecular weight by using GPC and chemical structure by using FTIR.
2. The effect of the mass ratio of sericin and LA monomer (2:98, 4:96, 6:94 and 8:92) on the solubility, %grafting, molecular weight and chemical structure of the sericin-g-PLA.
3. The effect of contents of clay (2-8 wt%), acrylic acid (2-8 wt%), plasma treatment times (15-120 seconds) and sericin and LA monomer ratio on the properties of sericin-g-PLA clay aerogel with acrylic acid such as the

morphology, mechanical and thermal properties by using SEM, compression testing and TG-DTA, respectively.

4. The possibility to use sericin-g-PLA clay aerogel with acrylic acid as ethylene scavengers for the packaging application by using GC and surface area analyzer.