

CHAPTER I

INTRODUCTION

Nowadays, natural polymeric materials have become increasingly important due to their natural abundance and low costs. Chitosan is the *N*-deacetylated derivative of chitin, though this *N*-deacetylation is almost never complete (Robert, 1992). Chitosan is known to be non-toxic, odorless, biocompatible with living tissues, biodegradable, and chemically functionalizable. Due to these advantages, chitosan and its derivatives are seen in applications such as biomedical materials, biodegradable packaging, cosmetics, metal ion-capturing materials for waste-water treatment, and so on so forth (Ravi Kumar, 2000).

Dissolution of chitosan in organic solvents is important in many applications. It is well known that chitosan is generally insoluble in many common solvents: water, alkali and organic solvents, but it is soluble in solutions of organic acids only when the pH of the solution is less than 6 (Muzzaerelli, 1977). Acetic and formic acids are two of the most widely used solvents for dissolving chitosan. However, these solvents offer very limited applications in producing chemical derivatives in homogeneous solution, in particular the large-scale applications. Poor solubility of chitosan in common organic solvents can be traced to its rigid crystalline structure through intramolecular and intermolecular hydrogen bondings (Roberts, 1992). This is the primary reason for limited useful chitosan applications. In order to solve this problem, some chemical modifications to introduce hydrophobic nature to chitosan such as phthaloylation (Nishimura *et al.*, 1991), alkylation (Yalpani and Hall, 1984), and acylation (Hirano *et al.*, 1976; Moore and Roberts, 1981; Zong *et al.*, 2000) reactions can be done. Organically soluble derivatives of chitosan can be used to formulate by-designed materials for biomedical applications such as polymeric drugs and artificial organs with high specificity and wide applicability.

Zong *et al.* (2000) synthesized three kinds of acylated chitosans by reacting chitosan with hexanoyl, decanoyl and lauroyl chlorides. In contrast to the chitosan, all of acylated chitosans showed excellent solubility in common organic solvents such as halogenated hydrocarbons and aromatic solvents such as chloroform, benzene, pyridine, and tetrahydrofuran (THF), but poor solubility in polar solvents.

N-acylchitosan has been fabricated as membranes (Seo *et al.*, 1995), fibers (Hirano *et al.*, 1998), and films (Xu *et al.*, 1996). *N*-hexanoyl chitosan was found to exhibit the best blood compatibility in comparison with *N*-propionyl, *N*-butyryl, and *N*-pentanoyl chitosans (Lee *et al.*, 1995). Furthermore, *N*-hexanoyl and *N*-octanoyl chitosans were found to be anti-thrombogenic and resistant to hydrolysis by lysozyme (Hirano and Noishiki, 1985). As a result, hexanoyl-chitosan (H-chitosan) is a very interesting derivative of chitosan to be used in biomedical applications.

Polymer blending is an attractive alternative for producing new polymeric materials with tailored properties without having to synthesize totally new materials. Other advantages for polymer blending are versatility, simplicity, and inexpensiveness. Among the various aliphatic degradable polyesters, polylactide (PLA) has been considered as one of the most interesting and promising biodegradable materials and has been used in medical applications, such as surgical sutures (Fambri *et al.*, 1997), drug delivery systems (Khang *et al.*, 2003), and bone fixtures (Bergsma *et al.*, 1996).

By blending PLA with other polymers, polymers with an improved range of applications are obtained. A number of studies have focused on the blending of PLA with other polymers or copolymers. These blends include PLA with poly(3-hydroxybutyrate), and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (Iannace *et al.*, 1994; Blumm and Owen, 1995), blends of PLA with poly(ethylene glycol) (Younes and Cohn, 1988), and blends of PLA with poly(ϵ -caprolactone) (Cha and Pitt, 1990).

Physical and mechanical properties of the blends are very much dependent on state of mix and miscibility between the constituent components as well as the phase morphology of the resulting blends. For solution-cast blends however, another important factor determining the final properties of the resulting blends is the choice of the casting solvent used to prepare the blend solutions for casting.

Even though a large number of studies on solution-cast polymer blends are available in the open literature, only limited number are dedicated to study the effect of casting solvent on properties of the resulting blends. Bank *et al.* (1971) showed that films of polystyrene (PS)/poly(vinyl methyl ether) (PVME) blends appeared to be compatible when either toluene or benzene was used as the casting solvent, and

they appeared to be incompatible when either trichloroethylene or chloroform was used. Asaletha *et al.* (1995) reported that the nature of the casting solvent had a profound effect on the compatibility behavior of natural rubber (NR)/polystyrene (PS) blends compatibilized by NR-g-PS. Radhakrishnan and Venkatachalapathy (1996) showed that the choice of the casting solvent used (e.g. dichloromethane, tetrahydrofuran, and toluene) to prepare the blend films of poly(ethylene oxide) (PEO) and poly(methyl methacrylate) (PMMA) not only affected the compatibility of the resulting films, but also the crystallization of PEO.

Recently, much attention has been paid to the electrospinning process which can produce polymer nanofibers with diameters typically in the range from 100 to 500 nm (Deitzel *et al.*, 2001; Doshi and Reneker, 1995). The electrospun fiber mats have distinctive properties such as high surface area-to-volume ratio, high porosity, and high absorption. The morphology of electrospun fibers can be varied according to electrospinning conditions, solvent and solution properties, and additive type.

This work investigated chemical modification of chitosan to prepare an organic solvent-soluble derivative of chitosan, hexanoyl chitosan (H-chitosan). H-chitosan was prepared by repeatedly reacting chitosan with hexanoyl chloride. Chemical structure and properties of the product were characterized. The solution properties of the H-chitosan dissolved in chloroform, dichloromethane and tetrahydrofuran were also investigated. There are many studies on for solution properties of chitosan. There have been reported that solution properties of chitosan depend on degree of deacetylation, solvent system and temperature (Gamzazade *et al.*, 1985; Wang *et al.*, 1991; Anthonsen *et al.*, 1993; Rinaudo *et al.*, 1993; and Ottey *et al.*, 1996). However, the study on solution properties of chitosan derivatives, especially acylchitosan, is rather rare. The investigation of solution properties of H-chitosan is interesting because these properties can reveal to the behavior of polymer in solvent. The present work focused on the dilute solution behavior of H-chitosan in organic good solvents, i.e. chloroform, dichloromethane, or tetrahydrofuran, which were investigated by viscometry and dynamic light scattering technique. Our results demonstrate the importance of solvent and polymer-solvent interactions and provide an explanation for some poorly understood experimental

observations in organic soluble chitosan derivatives studies. In addition, the study on the surface tension of H-chitosan in various organic solvents was also reported.

The blend of H-chitosan and PLA was prepared in two forms, films and fibers, by the solution-casting and electrospinning, respectively. The main objective of this part was to find an economical way for improving the applicability of H-chitosan through the blending with PLA. In case of the blend films, the effects of blend composition and casting solvent (chloroform, dichloromethane, or tetrahydrofuran) on miscibility, morphology, thermal properties, and mechanical properties were investigated. In case of the electrospun fibers, the morphological features of the electrospun H-chitosan/PLA blend fibers were investigated with different blend ratios and solvent.