

CHAPTER I

INTRODUCTION

Recently, polymeric chain layer has received much interest and been reported for its specific properties, such as chemisorption, physisorption, and controlled release system (Takeshi *et al.* (1998)). In most cases, the materials allow significant improvement in physical properties such as mechanical strength, thermal stability, gas permeability as well as the appearance due to the interactions at molecular level generated among polymer molecules (John *et al.* (2001)) or hybridization with inorganic molecules in each layer (Yang *et al.* (1997)). Crab and shrimp shells are one of the good examples of natural polymer system formed in layer structure which consists of chitin-chitosan, protein, and inorganic minerals (Berman *et al.* (1988)). It is also known that the layer structure of chitin-chitosan and protein is hardened by the function of calcium and magnesium.

For the past decades, the development of composites has become distinguished due to the well understanding of the structure of polymer chain with inorganic hybridization (Wilkes *et al.* (1990)). Nanocomposite is the most challenging to polymer chemists since it is an approach to achieve the miscible systems of organic-organic and organic-inorganic molecules whereas the unique physical and chemical properties can be expected (Pinnavaia *et al.* (1996)). Based on the nanolayer or nanochannel, clay (montmorillonite) is well accepted as an inorganic material appropriate for nanocomposites (Ruiz-Hitzky *et al.* (2002)) since it provides not only the layer in nanometer level but also the interaction with polymer chain via ionic interaction. It should be noted that the success of nanocomposite is so significant that Mitsubishi Engineering Plastics launches a series of gas barrier film for food packaging under the trade name of NOVAMID[®] (www.mep.co.jp/mep-en/index.htm).

Considering the crustacean shells and nanocomposites, we may claim that crustacean shell is a perfect bionanocomposite where multicomponent of chitin-chitosan, cuticle, protein and minerals co-exists with miscibility resulting in a material which possesses water-insolubility, high strength, and good mechanical properties with complete biodegradability. It is important to note that although

nanocomposite has received much attention and of become well understood at molecular level, up to now there is no report success in preparing artificial bionanocomposite similar to that of crustacean shell. The present project is thus based on the understanding of crustacean shell as bionanocomposite and aims to develop approaches for preparing chitosan nanocomposite. Considering the packing structure of chitin-chitosan with 1 nm layer thickness, one may easily understand how structure of chitosan layer is similar to that of Na^+ -montmorillonite (Scheme I). Here, chitin-chitosan is expected to provide a nanochannel to incorporate with other inorganic materials and/or polymer chains where the structure is well aligned either by ionic interaction or hydrogen bonding as well as other secondary forces. The present work is, thus, concentrated on (i) intercalation efficiency of chitosan for nanocomposite formation with organoclay (Chapter III), (ii) clarifying the synthesis pathways or preparation steps to accomplish the chitosan-clay oligoester nanocomposite of chitosan-clay nanocomposite obtained from (i) (Chapter IV), and (iii) clarifying the synthesis pathways or preparation steps to accomplish the chitosan oligo/polyester nanocomposite (Chapter V). The present work is a part of the project aimed at synthesizing the crustacean biomimic structured nanocomposites.

Scheme I

