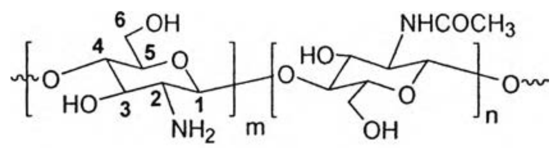
CHAPTER I
INTRODUCTION

Chitin-chitosan is well-known for the second most naturally abundant polysaccharide next to cellulose obtained from crustaceans, cuticles of insects, cell-wall of fungi and yeasts. It presents as a high molecular weight copolymer of β–(1-4)-2-acetamido-2-deoxy-β-D-glucose and β-(1-4)-2-amino-2-deoxy-β-D-glucose (Scheme 1.1).

Scheme 1.1 Chemical structure of chitin-chitosan copolymer



chitosan chitin

Chitosan exhibits many specific properties, i.e. (i) bioactivity (Dumitriu *et al.*, 1989), biocompatibility (Richardson *et al.*, 1999), and nontoxicity (Arai *et al.*, 1968) due to the pyranose ring; (ii) biodegradability owing to glycoside linkage (Yamamoto *et al.*, 1997); (iii) functionality due to amino group at C-2 and hydroxyl at C-6 position; (iv) metal ion adsorptivity (Peniche-covas *et al.*, 1987), antimicrobial, and antibacterial activities (Kendra and Hadwiger, 1984) due to its amino group. According to its unique biological activities, chitin-chitosan has a variety of current and potential applications in biomedical products (Kifune, 1992) such as cosmetics (Gross *et al.*, 1983), food processing (Knorr, 1985), etc. Its reactive amino and hydroxyl group have received much interest for chemical modification to develop several derivatives and value-added products. In comparison, chitosan have even more paid attraction over chitin since it provides both hydroxyl and amino groups for functionalization. In the earlier, the uses of chitosan are mainly focused on the physical modification such as casting to film (Puttipipatkhachorn *et al.*, 2001), crosslinking to gel (Hamdinea *et al.*, 2005), wet spinning to fiber (Lim and Hudson, 2004). In recent years, the advanced development of chitosan, e.g. hydrophilic or hydrophobic drug molecules (Yoksan *et* *al.*, 2003), chitosan-sugars nanoscaffold (Phongying et al., 2006), and chtiosan nanosphere (Rangrong *et al.*, 2004), water soluble chitosan (Fangkangwanwong *et al*, 2006), etc., have been reported. Most of the previous reports in chitosan technology based on its own value-add by chemical modification and use with the specific applications.

At the present time, to consider chitosan as a bio-additive for value-added commercial polymer has received much attention. Based on the fact that chitosan exhibit several useful and specific properties, using chitosan bio-additive combined with commercially synthetic polymer can promote the new function of chitosan to commodity polymer. Chtiosan surface functionalization is an approach to introduce the unique properties of chitosan onto polymer substrate because it is known as a practical way to provide polarity and hydrophilicity to a polymer surface. Chitosan derivatives, such as O-Butyrylchitosan (OBCS) and chitosan 4-azidobenzoic acid (Mao *et al.,* 2004) have been reported as bio-additives for surface functionalization for blood compatibility material in biomedical application.

In another view point, chitosan bio-additive based antioxidant has also been paid attention as the demand for natural antioxidant is increasing to alternate the traditional synthetic antioxidant. Recently, much effort has been applied to consider chitosan as a natural antioxidant, for example, chitosan sulfate derivatives (Xing *et al.*, 2004; Xing *et al.,* 2005) maleic acid grafted onto hydroxypropyl chitosan or carboxymethylchitosan (Xie *et al.,* 2001), and schiff bases of chitosan (Guo *et al.*, 2005). However, the development of chitosan to serve as an antioxidant for commodity polymer is rarely found.

The present dissertation originally focuses on the specific development of chitosan based bio-additive. The bio-additive materialization of chitosan studied by two approaches, i.e. (i) chitosan bio-additive for surface functionalization, and (ii) chitosan bio-additive based antioxidant for commodity polymer. According to the literature report in the case of (i), only the biocompatibility is mainly considered when introducing chitosan onto polymer surface. The present work focuses on another view point for chitosan surface functionalization based on the metal ion chelating ability of chitosan for value-added polyethylene. In this way, chitosan is functionalized onto polyethylene film via γ-ray irradiation in aqueous solution to prepare chtiosan-copper ion complex based commodity polymer. In the case of (ii), the conjugation of gallic acid and deoxycholic acid to chitosan is an attractive approach to achieve the antioxidant anchoring polymer for commodity polymer. The present work also covers the clarification of antioxidative activity by using the electron paramagnetic resonance (EPR) spectroscopy for free radical characterization.