

CHAPTER II

LITERATURE SURVEY

2.1 Chitin in Polymer Blends

Aoi *et al.* (1995, 1997) indicated that a chitin derivative having poly (2-alkyl-2-oxazoline) side chain showed much improved solubility and good miscibility toward PVA over the entire composition range.

Lee *et al.* (1996) studied mechanical properties of blend films of β -chitin and PVA. It was found that tensile strength of the blend was greater than that of both homopolymers. Upon mixing with PVA, the tensile strength decreased and elongation at break increased with PVA content. By visual inspection, there was no evidence of phase separation in any of the blend compositions. The transmission electron micrographs of the blend that contained 70% of chitin showed some microseparations, but it was still believed to be miscible in the blend.

Arvanitoyannis *et al.* (1997) reported physical properties of highly deacetylated chitin/PVA blends plasticized with sorbitol and sucrose. These films showed an increasing in CO₂ and water vapour permeability with an increasing in plasticizer content. However, high plasticizer content caused a substantial decrease in both tensile strength and modulus.

Since chitin is a biodegradable resource, it can be blended with commodity polymers to enhance their degradability in the environment as reported by Makarios-Laham and Lee in 1995. They studied the biodegradation of polyethylene-chitin and polyethylene-highly deacetylated chitin blend films, containing 10% by weight of chitin and its derivative. After six months of incubation in soil, it was found that 100% of both chitin and its derivative in the films were degraded.

2.2 Starch as a Filler in Polymer Blends

In 1973, Griffin first reported the degradability of polyethylene/starch composite films containing 6-10% of starch content. The degradation rate was accelerated by adding an autooxidant such as unsaturated fatty acids to the system. The use of starch as a biopolymer filler in polymer blends has been studied extensively since then.

Winlett (1994) studied the mechanical properties of composites of granular starch and low-density polyethylene (LDPE) as functions of starch volume fraction, granule size and the addition of compatibilizer. Results were discussed in terms of elongation, tensile strength and modulus of starch-filled composites. The elongation and tensile strength decreased with increasing starch volume fraction in agreement with theoretical predictions. The modulus of the composites increased with increasing starch volume fraction. The addition of ethylene-*co*-acrylic acid copolymer as a compatibilizer had no effect on elongation and tensile strength, but significantly increased the modulus of composites. Potato starch/LDPE composites, which has the larger particles than corn starch, had lower tensile strength and modulus than corn starch/LDPE composites. In addition, particle size had no effect on elongation.

Kim *et al.* (1995) modified the starch with commercial ionomer, Surlyn, to improve the compatibility with LDPE. The mechanical and rheological properties were examined for the blends of the modified starch and LDPE. Tensile strength tended to increase with increasing starch content because the starch particles reinforced the polymer matrix. In contrast, percent elongation decreased abruptly as starch was added. From the rheological study, LDPE blended with modified swollen-starch offered good compatibility. Besides, the fungal degradability test verified the biodegradability of the blends.

Bhattacharya *et al.* (1995) reported that the addition of starch to ethylene-propylene- *g*-maleic anhydride (EPMA) caused slightly reduction in tensile strength and significant reduction in percentage of elongation. For starch/styrene-maleic anhydride (SMA), the addition of starch reduced the tensile strength while the percentage of elongation was unaffected. Water absorption of starch/EPMA blends was higher than that of starch/SMA blends.

Nakashima and Matsuo (1996) improved the strength of corn starch treated with silane coupling agent and ultrahigh molecular weight polyethylene composite films by varying the composition of the films. The drawability became less pronounced as the starch content increased. However, the mechanical properties of the composite films improved dramatically in comparison with undrawn composite films with 10% starch content produced in a pilot plant. The test of microbial degradation of the films was carried out by using fungi. Observation by SEM revealed that the number of starch particles between polyethylene matrix decreased drastically and the average size of residual particles was smaller, indicating their effective biodegradation result.

Kang *et al.* (1996) improved the physical properties of starch-filled polyolefins by introduction of cholesterol, hydrophobic unit into starch. At higher starch content, HDPE/modified starch films showed higher tensile strength, elongation and more dispersion and adhesion than HDPE/native starch. Moreover, modified starch-filled HDPE films could increase the biodegradable component without adversely affecting the physical properties of the films.

Thiebaud *et al.* (1997) reported that the esterification of starch with fatty acid esters increased thermal stability and enhanced its thermoplastic character and mechanical properties. The starch octanoate and dodecanoate were mixed LDPE at various proportions. The blends of LDPE with starch

esters retained satisfactory mechanical properties and improved thermal stability for starch ester contents up to 15-20%.

Suranakapan (1998) reported the processability and mechanical properties of HDPE film containing starch as a filler. Two types of native starch, rice starch and tapioca starch, were used. Torque measurements during the blending process suggested that the addition of starch filler stiffened the blends. In addition, tapioca starch provided more homogenous blends with better dispersion and more uniform distribution of the starch particles than the rice starch. Mechanical properties of starch-based HDPE blown films were measured as a function of starch content. With increasing starch content, there was a decrease in tear resistance, tensile strength and elongation at yield with the exception of tear resistance of tapioca starch-based HDPE blown film at low starch concentrations where tear resistance was found to increase with increasing starch content up to a maximum loading of 7.5%. Mechanical properties of rice starch-based HDPE blown films were strongly influenced by rice starch agglomerate structure.

Recently, Bikiaris *et al.* (1999) blended LDPE with different amount of fatty esters of amylose and starch. It was found that the blends had unsatisfactory mechanical properties at higher ester concentrations. That was due to the poor interfacial adhesion between LDPE and the esters, which resulted in an incompatible system, as noticed by SEM.

2.3 Other Fillers in Polyethylene Blends

Incorporating of particulate fillers into polymers is well known that this can change the properties of polymer such as physical and mechanical properties.

Chow (1982) developed the equation to predict the ultimate tensile strength of a particulate-filled polymer. These equations did not depend only on the volume fraction of the filler and the elastic modulus of two material

phases, but also on shape, size and interfacial adhesion between the filler and the matrix. From this model, the ultimate tensile stress increased and the ultimate strain decreased with an increase of either the aspect ratio or the volume fraction of the filler. When the particle size was greater than a critical value, the ultimate tensile strength decreased as the size of filler particles increased. The prediction of the model showed reasonably good agreement with published experimental data.

Tavman (1996) reported mechanical properties of aluminum powder filled HDPE composites. It was found that filler tended to form agglomerates at higher particle content (greater than 20%). Tensile strength and elongation at break decreased with increasing aluminum particle content, which was attributed to the introduction of discontinuities in the structure. For particle content higher than 30%, a decrease in the modulus of elasticity was observed which may be attributed to the formation of cavities around filler particles during stretching in tensile test as notice from microscopic studies.

In 1997, Mlecnik and La Mantia studied the mixing of different polyolefins, several calcium-based fillers and sunflower oil. They studied on the effect of viscosity and type of polyolefins on Young's modulus, yield stress, and elongation at yield. Four types of polyolefins studied were low- and high-viscosity HDPE and polypropylene (PP) and four types of fillers were two different sizes of CaCO_3 , a stearate-coated CaCO_3 and a building grade CaCO_3 . The influence of the filler content showed that the yield properties decreased with increasing filler content while elastic modulus increased. Polyolefins filled with the larger size particles gave similar tensile strength and improved elongation at yield and modulus when compared to those filled with smaller size fillers. The lubricating effect of sunflower oil gave rise to an increase of elongation at yield due to the easier slippage of the macromolecules. SEM micrographs showed the formation of agglomerates and filler/matrix adhesion.

Bartczak *et al.* (1999) improved toughness of HDPE by the adding of rigid particulate fillers consisting of three different sizes of CaCO_3 particles. Mechanical properties of the compounds were also examined as functions of filler particle size and filler volume fraction. While the use of CaCO_3 particles as toughness promoting agent increased toughness, they also improved impact energy and degree of crystallinity. Moreover, Young's modulus of the blends increased with increasing concentration of CaCO_3 while the yield stress gradually decreased. Comparison of moduli of the blends with different CaCO_3 showed that the filler with larger particles caused a slightly greater increasing of the moduli than those with smaller particles.