CHAPTER III
EXPERIMENTAL SECTION

3.1 Materials

3.1.1 Polymer Matrix

High density polyethylene (HDPE) was kindly supplied by Bangkok Polyethylene Co., Ltd. with trade name Thai-zex® 7000F. It was appropriate for packaging application. The melting point and the softening point were 131°C and 124°C, respectively. The melt flow rate at 2.16 kg/190°C was 0.04 g/10 min and the density was 0.956 g/cm^3.

3.1.2 Biodegradable Filler

The tapioca starch was kindly supplied by Siam Modified starch Co., Ltd. Normally, starch consists of amylose and amylopectin. The density of starch was 1.45 g/cm^3. The particle shape of tapioca starch is spherical with 10-15 μm size.

3.1.3 Autooxidant

Natural rubber (TTR5L) was supplied by Victor & Prosper Limited Partnership. It was used to promote the oxidative degradation of the blends.

3.1.4 Prooxidant

Zinc stearate [$Zn(C_{17}\ H_{35}COO)_2$] was supplied by Imperial Industrial Chemicals (Thailand) Co., Ltd. It was used as a transition metal to catalyze the oxidative degradation of HDPE. The melting point was 120-124°C and the metal content was 10.0-11.5%.

3.1.5 Compatiblizers

Three types of compatibilezers, including poly(ethylene-*co*-acrylic acid) (EAA), poly(ethylene-*co*-vinyl acetate) (EVA), and polyethylen-*graft*-maleic anhydried (PE-*g*-MA), were purchased from Aldrich Chemical Company, Inc. They were used to study the effect on the oxidative degradation of HDPE. The density of EAA, $[-CH_2CH_2-]_x[-CH_2CH(COOH)]_y$, and EVA, $[-CH_2CH_2-]_x[CH_2CH(OOCCH_3)]_y$, were 0.96 and 0.94 g/cm^3, respectively. PE-*g*-MA has density 0.92 g/cm^3.

3.1.6 Enzyme α-Amylase

The enzyme α-amylase, Termamyl, was obtained from Novo Industry. Termamyl is a liquid enzyme preparation containing an outstandingly heat-stable α-amylase expressed in and produced by a selected strain of *Bacillus licheniformis*. The enzyme is an endoamylase which can hydrolyze (1-4) α-glucosidic linkage in amylose and amylopectin. Starch is therefore rapidly broken down to soluble dextrins and oligosaccharides.

Activity of enzyme was defined in term of Kilo Novo α-amylase Unit (KNU). 1 KNU is the amount of enzyme which breaks down 5.26 g starch per hour at Novo Nordisk's starndard method for determination of α-amylase.

3.2 Blends Preparation

The blends containing different additive were prepared to study the effect of each component to the degradation. The components are shown in Table 3.1.

The tapioca starch was dried in a hot air-oven at 110°C for 2 hours to reduce moisture content. The natural rubber was masticated on two-roll mill for 10 min prior to use. The blends were mixed on a Lab Tech LRM 110 two-roll mill for 15 min. Three different levels of starch used were 5, 10 and 20 wt%. Zinc stearate was used as a prooxidant at a quantity of 1% by weight based on total weight. The compatibilizer concentration was kept to a constant 10 wt% based upon starch.

Table 3.1 The blends containing various additives

Component	HDPE	ZnSt	NR	starch	compatibilizers
A	100	-	-	-	-
B	99	1	-	-	-
C	95	-	5	-	-
D	94	1	-	5	-
E	89	1	-	10	-
F	79	1	-	20	-
G	94	1	5	-	-
H	89	1	10	-	-
I	98.5	1	5	5	0.5
J	83	1	5	10	1
K	72	1	5	20	2

* The abbreviations ZnSt and NR refer to Zinc stearate and natural rubber, respectively.

After mixing, the blends were fed into a shredder followed by compression molding using a Wabash V50H Press. The compression molding was performed at 170°C for 3 min and forced with 10 tons force for 1 min before being cooled down to room temperature. Both sheets and the films were produced. The sheets were press-cut to prepare dumbbell specimens for further study.

3.3 Degradation Procedure

3.3.1 Part I : Thermooxidative Degradation

The oxidative degradation was performed in an air circulation oven. Laboratory air circulation oven model UT6, at 75°C. The aged dumbbell specimens and films samples with 100 ± 10 μm were incubated for several days and were removed at regular time intervals in order to monitor any changes in mechanical properties and chemical changes. Upon completion of chemical change measurement, the film samples were placed back in the oven.

3.3.2 Part II : Enzymatic Degradation

The 15x15 mm films with approximate weight 0.015-0.025 g were treated with enzyme α-amylase in acetate buffer solution. The treatment was performed in 25 ml of 0.05 M acetate buffer pH 6 with 54 mM $CaCl_2 \cdot H_2O$ at 60°C with shaking in a water bath. A similar sets were prepared in the same manner except without enzymes to use as a control. The samples were removed to determine weight changes and the percentages of starch hydrolysis were calculated. The microstructures of the blends before and after the treatment were observed by using the scanning electron microscope (SEM).

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$$CI^{C} = CI - CI^{0}$$

In this work, the CI was corrected by subtracting the CI before incubation to get a value which depended only on carbonyl newly formed.

3.4.4 Scanning Electron Microscopy (SEM)

The changes in the surface morphology of the blends before and after starch hydrolysis by enzyme α-amylase were observed by using a scanning electron microscope model JEOL JSM 5200. The surfaces of the blends were coated with gold prior to examination. The operation voltage was set at 1 kV and the magnifications was set to 200X and 350X.