

## CHAPTER III

### LITERATURE REVIEW

A majority of the current research on plastic additives aim to study the stabilizing efficiency of various antioxidants in a polymer matrix. This chapter will emphasize on some review of literatures on polymer degradation, stabilizer systems and related topics.

Yan Qing and Xu Wenying [9] analyzed the changes of the surface, bulk structures and the properties of crosslinked and uncrosslinked polyethylene when the PE was exposed to simulated sunlight and elevated temperatures. It was found that the UV-irradiation during crosslinking process decreases the stability of PE considerably. Two kinds of antioxidants (hindered phenol and thioester) were used in conjunction with a photostabilizers (hindered amine), which all of them have no absorption in the UV region of 300 to 400 nm, they were added before crosslinking to improve the stability of the crosslinked PE in several formulae. The results of surface analysis showed that there was "pre-oxidation" during photo-irradiation when the PE was crosslinked. The pre-oxidation causes a shortening of the oxidative induction time of the photocrosslinked PE. For the same reason, the crosslinked PE would be expected to oxidize more deeply and be destroyed more quickly in the weathering test than the uncrosslinked ones. The hindered amine studied was the most efficient stabilizer for photocrosslinked polyethylene against photooxidation in the weathering tests. Its addition made the crosslinked PE retain its gel content and tensile properties for quite a long

weathering period. On the other hand, the hindered phenol and the thioester studied showed a strong synergism on antioxidation at an elevated temperature in the oven test.

E. G. Kolawole and G. Scott [10] improved the thermal and photo-oxidative performance of ABS by using antioxidant and UV stabilizer masterbatches as conventional additives for normal ABS. The ABS masterbatches, ABS(M<sub>1</sub>) and ABS(M<sub>2</sub>), containing high concentration of 3,5-di-*tert*-butyl-4-hydroxybenzylmercaptan (BHBM) and 4-benzoyl-3-hydroxyphenyl *O*-ethylthioglycollate (EBHPT) respectively, were prepared by grafting the antioxidant and UV stabilizers onto ABS in the latex phase. The commercial stabilizers used were UV 531 and hindered amine. The induction periods and embrittlement times were found to depend on the concentration of the added masterbatches reaching a maximum at 2% addition. In the case of the synergistic mixtures, the mixture containing 2% bound EBHPT in ABS(M<sub>2</sub>) and 1% BHBM bound in ABS(M<sub>1</sub>) gave the best performance under UV irradiation, where the mixture containing 1% EBHPT bound in ABS(M<sub>2</sub>) and 1.5% BHBM bound in ABS(M<sub>1</sub>) gave the best performance when heated in an air oven. The combination of UV absorber and antioxidant gave a very good stabilizing effect for ABS.

R. Chandra [11] improved the thermal and photo-oxidative stability of commercial styrene-butadiene copolymer (SBR) films in the presence and the absence of ferric stearate as an oxidation accelerator. The results were then compared with that of SBR in which a synergistic mixture of an antioxidant 3,5-di-*t*-butyl-4-hydroxybenzylmercaptan (BHBM) in combination with a stabilizer 1,1,5-triphenyl-2-S-(3',5'-di-*t*-butyl-4'-hydroxy)benzyl-iso-4-thiobiuret (PBHBT)

bounded in the SBR. A comparison of the resulting molecular weight, degree of degradation, gel content, elongation at break, density, hydroperoxide, carbonyl and hydroxyl groups of a SBR without ferric stearate and without BHBM/PBHBT showed that the effectiveness of the BHBM and PBHBT stabilizers was sufficient for SBR in the presence and the absence of ferric stearate. The physical, mechanical and chemical properties were found to depend on the concentration of the added stabilizers. The photostabilizer as well as a metal deactivator PBHBT has been found to possess a very high efficiency in SBR. In the case of synergistic mixtures, the mixture containing 0.5 wt.% BHBM and 1.0 wt.% PBHBT in SBR gave the best performance under processing and 365 nm irradiation in air at 90°C.

M. L. Berlanga-Duarte, J. L. Angulo-Sanchez and M. C. Gonzalez-Cantu [12] reported the analysis of the combined action of four additives on the accelerated UV degradation process of LDPE films, formulated with two photostabilizers (hydroxybenzophenone and hindered amine) and two antioxidantants (hindered phenol and phosphite). The degradation process is evaluated by measuring the changes in chemical structure (carbonyl evolution, chain scission and recombination) as well as the loss in mechanical characteristics such as tensile properties. A series of 33 formulations with different additive ratios, concentrations and a blank were designed, using a faced-centered-composite experimental design. From each formulation, films of 200  $\mu\text{m}$  in thickness were produced by extrusion-blowing process. The results of UV-accelerated aging, measured as the elongation at break ( $E_B$ ) reduction in polyethylene films formulated with four additives (two synergistic pairs), were, in general, similar to those reported for the individual additives as far as the shape of the  $E_B$  versus time curves was concerned. The half-

lifetimes, defined as the time required to reduce  $E_B$  to half its initial value showed a tendency to increase upon increasing the total additive concentration. However, different values of half-lifetime were obtained for the same total additive concentration which was due to the different amount of antioxidants and UV additives. In some cases, the influence of the additive ratio was stronger than that of the concentration. The half-lifetimes for the different formulations studied were found to be a function principally of the additive combinations rather than the total additive concentrations. This reflected the significance of the interaction between the antioxidants and the UV photostabilizers.

Yong Lie Chen, Bengt Ranby [13] studied the thermal oxidative stability of photocrosslinked high density polyethylene. The relative effectiveness of various antioxidants (hindered phenols and amines, aromatic amine, organic sulfides, and phosphites) was examined by comparing the oxidation induction time (OIT) which was measured using a Differential Scanning Calorimetry. Hindered phenol antioxidants were found to be most effective. At an antioxidant concentration of 0.20 wt%, which gave an OIT value of 20 min at 200°C, the photocrosslinking rate was decreased only to a limited extent. This was evidenced by a small drop in gel content. However, the efficiency of the antioxidants as stabilizers decreased to a considerable extent after the photocrosslinking process. Serious surface deterioration was found which was ascribed to the depletion of antioxidant at the surface mainly due to the high rate of oxidation and evaporation. A combination of hindered phenol and the organic phosphite gives the strongest synergistic effects. An OIT of 28 min was obtained using 0.15 wt% of each component but the ease of hydrolysis of phosphites could be detrimental in certain applications.



N.S. Allen, *et. al* [14] prepared and characterized three light stabilizers, based on the substitution of a tertiary amine group into the 3- and 5-positions of 2,4-dihydroxybenzophenone (DHBZ) and 2-hydroxy-4-n,octoxybenzophenone (HOBZ) via the Mannich reaction. The derivatives prepared by this method were, the 3-N,N-diethylaminomethyl of the former and the 5-N,N-diethylaminomethyl and 5-morpholinomethyl derivatives of the latter. The thermal and photo-oxidative stabilization activities of the three compounds were examined and compared with those of DHBZ and HOBZ in medium density polyethylene and polypropylene films at 0.1% w/w concentration by using IR absorption, fluorescence spectroscopy and hydroperoxide analysis. In medium density polyethylene, all three aminated derivatives were found to be weak antioxidants with the diethylaminomethyl derivative of DHBZ being the most effective. The commercial light stabilizers, DHBZ and HOBZ, were also weak antioxidants and were less effective than the aminated derivatives. In polypropylene, similar results were obtained but both the derivatives of HOBZ (5-morpholino-HOBZ and 5-N,N-dithylamino-HOBZ) were effective. In the presence of a hindered phenolic antioxidant, all the stabilizers except the HOBZ were synergistic in the thermal oxidation of polyethylene whereas in polypropylene the effects were antagonistic. For photo-oxidation, the effects were found to be reversed with antagonism being observed in the case of polyethylene and synergism in polypropylene but only in the case of the morpholinomethyl derivative of HOBZ. The three aminated derivatives were found, unexpectedly, to be less effective as light stabilizers than the two simple commercial benzophenone stabilizers, HOBZ and DHBZ. Hydroperoxide formation was markedly reduced on oven-ageing of polypropylene by the aminated derivatives and was consistent with the ability

of the tertiary amine group to scavenge oxygen and free radicals. Fluorescence quenching studies on the same polymer also showed that the aminated derivatives were more effective quenchers than the corresponding commercial HOBZ and KHBZ stabilizers.

I. Bauer, E. D. Habicher, S. Komer, S. Almalaika [15] studied the behavior of mixtures of hindered amine light stabilizers (HALS), their nitroxyl radical, and alkylamine analogues, with aromatic and aliphatic phosphites during photooxidation of polypropylene (PP). The photostabilizing performance of the above mixtures of stabilizers was compared with that of the individual antioxidants and with the performance of a number of synthesized bifunctional stabilizers containing aromatic phosphite or phosphonite and either of the above HALS or related functions in the same molecule (referred to as "HALS-Phosphites" or "HALS-Phosphonite"). Combinations of the hindered aryl phosphite with the hindered amine, the tertiary amine and the bis-nitroxyl-analogue of hindered amine, gave antagonistic effects at most molar ratios examined. Furthermore, in all cases, the extent of antagonism was reduced with increasing the amount of the hindered aryl phosphite in the mixtures. Combination of the aliphatic phosphite, trilaurylphosphite, TLP, with the hindered amine in PP, on the other hand, has shown synergistic effect under photooxidative conditions. The HALS-Phosphites and HALS-Phosphonite examined have shown better stabilizing efficiency than the corresponding mixtures of the individual stabilizers.

K. Jirathanasathian [16] studied several the influences of chemicals and the dosages on both chemical and physical properties of the automotive inertube compound. Statistical experimental design was applied to minimize the numbers of experiments while the results achieved were still reliable and statistically conclusive. Central Composite Rotatable (CCR) design was chosen in order to study the effects of the dosage of three chemicals upon the formulation of automotive inertube compound. The chemicals were carbon black which acts as a filler, naphthanic oil which serves as a plasticizer and insoluble sulphur which is a vulcanizing agent. Five levels of dosage of each chemical were studied. In total, twenty formulae were prepared and tested. Multiple regression analysis and Response Surface Methodology (RSM) at 97.5% confident analysis of variance were performed. The result of the design can be analyzed statistically. Regression analysis and the analysis of variance test the suitability of the model of response surface equation in order to get the response surface equation with statistical confidence. This can create response surface and contour curve showing the relationship between the properties of compounded and chemicals quantities.