

Studying and Increasing Light Stability of Rotomolding Grade of Polyethylene

E. Feyz,^{1,2} N. Sharifi Sanjani,¹ H. Shahraki,² A. Ranji,¹ N. Ala^{1,2}

¹Faculty of Science, Tehran University, Tehran, Iran

²C.O.R&D Group, Research and Technology Company, National Petrochemical Company, Tehran, Iran

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ABSTRACT: This article covers the state-of-the-art light stabilizer for rotational molding and the influence of synergistic effects between light and thermal stabilizers, which improve physical and mechanical properties. Different formulations of polyethylene (PE) with light stabilizer, thermal stabilizer, and acid scavenger have been produced in twin-screw extruder. To study the light stability, sheets that pro-

duced by injection-molding machine have been put in weather-ometer instrument for 1000 h. After and before that, physical and mechanical properties have been evaluated. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 1590–1593, 2008

Key words: hindered amine light stabilizer; rotational molding; antioxidant

INTRODUCTION

Polymer degradation is the result of chemical irreversible reactions or physical changes that lead to the premature failure of the material. The deterioration of being exposure to UV radiation is one of the drawback causes of plastics, which is used in outdoor applications.

The photochemical degradation of polyethylene (PE) is a result of a free-radical auto-oxidation mechanism,¹ which leads to loss or changes in physical mechanical properties and discoloration of polymer. This cyclic process, as shown in Figure 1, is characterized by two features: autocatalysis and inhibition by additive.²

Light stability of rotational-molding grades is very important, because, in many cases, the rotomolded part's end use is as an outdoor product; for example, playground equipment, tanks, and kayaks.

The processing conditions are quite different from the other applications. The polymer is exposed to high temperature and long cycle times in an oxygen-rich environment. Thermal and light stabilizers protect polyolefins against oxidation²; but, in this work, we focus on light stability in side of thermal stabilizer.

Different types of light stabilizer are used. One of the important stabilizers is hindered amine light stabilizer (HALS). In the beginning, only low-molecular mass HALS was available. To overcome some disadvantages

associated with low-molecular mass stabilizers, for example, high migration rate and moderate resistance to extraction, polymeric HALS were developed.

Advantages of high-molecular mass HALS, becoming increasingly important in the last years, are due to their remarkable share to long-term light and thermal stability of polyolefines.

HALS structural variables, which affect performance, are molecular weight and molecular weight distribution, where the latter product is an oligomeric mixture, solubility in the intended matrix, compatibility with the matrix, inherent light stability of the supporting structure, and, in some cases, the molar concentration of active sites.³

EXPERIMENTAL

Apparatus

Turbomixer from Borhan Poya with 5500 rpm and capacity of 1.5 kg in 2 min mixing, twin-screw extruder from Dr. Collin, injection-molding model Sintesi 75 from Biraghi Monza, Weather-Ometer Instrument Model QUV produced by Q-panel, following the ASTM D4329-92 (using a fluorescent bulb UVB irradiance at 313 nm, with cycles of UV irradiance and a temperature at 60°C lasting for 8 h and an additional period with a spray of deionized water and a temperature at 50°C lasting for 4 h.) Tensile instrument model LR10k produced by LLOYD following the ASTM D638, impact strength instrument model 6545 produced by CEAST following the ASTM D256, Spectrophotometer model MinoLTA, following the ASTM D1925-70, was used in this study.

Correspondence to: E. Feyz (EL5810@Yahoo.com).

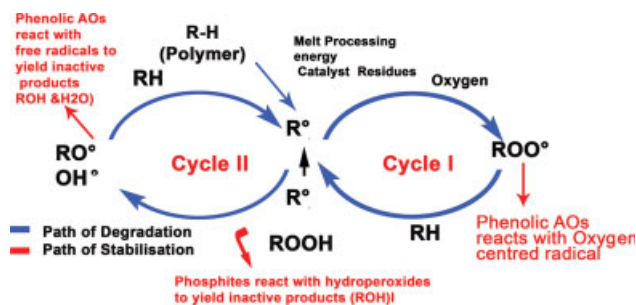


Figure 1 Autooxidation cycle for polymers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Materials

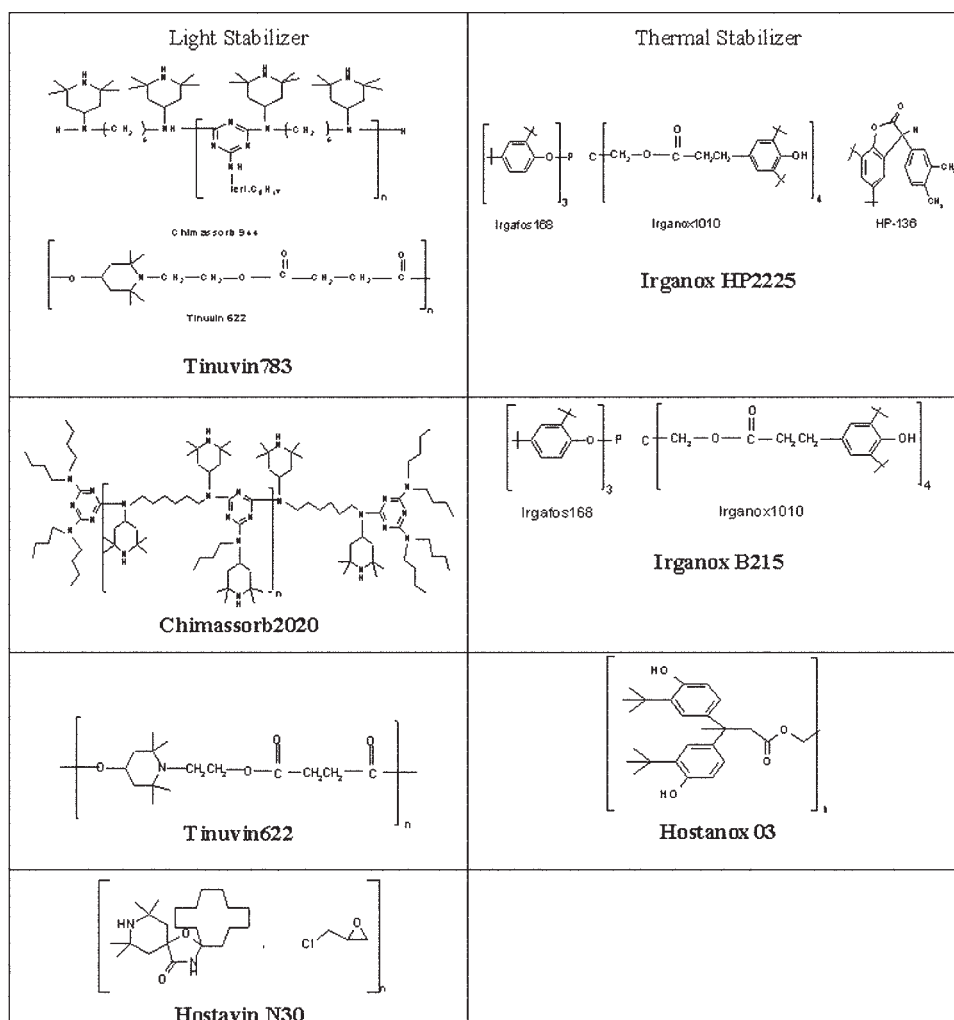
Unstabilized PE powder (Tabriz Petrochemical, Tabriz, Iran), light stabilizers Tinuvin 783, Tinuvin 622, Chimassorb 2020 (Ciba Specialty Chemicals, Basel, Switzerland), Hostavin N30 (Clariant, City, Country), antioxidants Irganox HP 2225, Irganox B215 (Ciba Specialty Chemicals), Hostanox03 (Clariant), Irgafos

168 (Ciba Specialty chemicals), and calcium stearate (Tabriz Petrochemical) were used (Scheme 1).

Procedure

Formulation of compounds is listed in Table I. In this study, we used 0.2% of light stabilizer and 0.1% of thermal stabilizer. Regarding the data in technical report of Ciba Company⁴ and some references as well,^{4,5} concentration of 0.2% is selected for Tinuvin 783 and already 500–1000 ppm of Irganox 1010 provide long-term thermal stability to the polymer.⁴

We should take into account that we have 0.1% Irgafos 168 and 0.1% Ca stearate in all formulations. Irgafos 168 is a hydrolytically stable phosphite-processing stabilizer. As a secondary antioxidant, Irgafos 168 reacts during processing with hydroperoxides formed by the autoxidation of polymers, preventing process-induced degradation and extending the performance of primary antioxidants.⁴ Ca stearate is acid scavenger and inhibits polymer from degradation



Scheme 1 Structure of polymer additives used in this study.

TABLE I
Formulation of Compounds

No.	Light Stabilizer(A) 2000 ppm	Thermal Stabilizer(B) 1000 ppm
1	Chimassorb2020	Irganox HP2225
2	Chimassorb2020	Irganox B215
3	Chimassorb2020	Hostanox03
4	Chimassorb2020	-
5	Tinuvin622	Irganox HP2225
6	Tinuvin622	Irganox B215
7	Tinuvin622	Hostanox03
8	Tinuvin622	-
9	Tinuvin783	Irganox HP2225
10	Tinuvin783	Irganox B215
11	Tinuvin783	Hostanox03
12	Tinuvin783	-
13	Hostavin N30	Irganox HP2225
14	Hostavin N30	Irganox B215
15	Hostavin N30	Hostanox03
16	Hostavin N30	-

effects of acidic compound that produces from catalyst of PE in the processing of polymer.⁶

For preparation compounds, according to additives and their percentages, which are available in Table I, additives combined with PE powder by mixer. Then, powder combinations produced by twin-screw extruder changed to granule. The conditions of extruder are shown in Table II.

Then, the obtained granules changed to sheets with dimensions of (4 × 65 × 130 mm) by injection molding.

RESULTS AND DISCUSSION

The comparison of physical mechanical properties of compounds before and after 1000-h exposure is shown in Figures 2–5. Because all HALS products contain nitroxyl (active site), the different performance that is obvious in various HALS is related to their differences in physicochemical properties.

Tinuvin 783 includes two light stabilizers: Tinuvin 622 and Chimassorb 944, with the ratio of 1 : 1. It is obvious that there is the best synergism result in combination with two polymeric light stabilizers in light and thermal stability.

Tinuvin 622 is a kind of polymeric and tertiary amine. All tertiary amines similar to nitroxides have the ability of quenching singlet oxygen, but secondary amines do not have this ability.⁷ The basicity and nucleophilicity of secondary amine HALS can sometimes contribute to undesirable side reactions.³

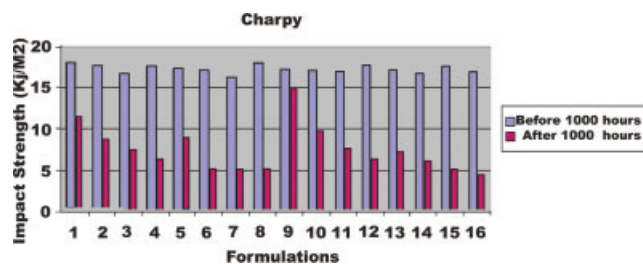


Figure 2 Comparison of impact strength between compounds after and before 1000-h exposure. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

To generate the active species for radical trapping in Tinuvin 622, the polyester HALS must first begin to self-destruct. Because the piperidinyl moieties are bonded to electron-withdrawing groups, the activation kinetic is not as favorable as they would be for a secondary or simply alkylated tertiary piperidinyl group.^{8,9} Because of this reason, surface protection is preferred. In addition, the polyester backbone is prone to photolytic and hydrolytic-cleavage reactions, which lead to additive loss. The latter reactions can be accelerated in the presence of typical formulation components such as stearates.³ Presence of Chimassorb 944 compensates deficiencies of Tinuvin 622. Chimassorb 944 is also a kind of polymeric light stabilizer, which has triazine backbones in its structure. Triazine backbones are excellent carriers for piperidinyl groups, affording superior thermal and photochemical stability as well as low volatility.³

Regarding to this fact that molecular weight of Chimassorb 944 is less than Tinuvin 622, the probability of migration of Chimassorb 944 is low and causes necessary light and thermal stability in high thickness. Compound having only Tinuvin 622, for the reasons which are explained before, will not provide suitable light stability in polymer.

Molecular weights of Tinuvin 622 and Chimassorb 2020 are similar to each other,⁴ but when two different stabilities by them are seen, we can understand that those have different solubility parameters make different effects on their performances. Presence of alkyl sections at the end of Chimassorb 2020 in comparison with Tinuvin 622 causes it to be more compatible with PE. For this reason, Chimassorb 2020 provides more suitable light stability than Tinuvin 622.

Hostavin N30 is an additive with low molecular weight. One of the factors that decrease the performance of additive is volatility from polymeric

TABLE II
Specifications of Extruder

Company	L/D	Feeder (rpm)	Extruder (rpm)	Cutter (rpm)	Zone's temperature (°C)
Dr Collin	18	150	60	740	180-190-200-220-210-200

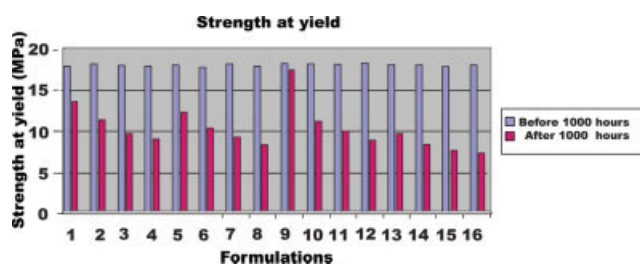


Figure 3 Comparison of strength at yield between compounds after and before 1000-h exposure. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

matrix.¹⁰ This factor is a reason for low performance of Hostavin N30 in comparison with others.

Trend of changing in mechanical properties such as impact strength, elongation at break, and strength at yield are similar. All show that, Tinuvin 783, for the reasons that explained previously, is the best light stabilizer. In the view of yellowness index, Tinuvin 622 is better than the others a little. Wholly, the formulation that includes basic additives such as light stabilizers causes discoloration in polymer greatly. The role of secondary amine light stabilizers in increasing discoloration by phenolic antioxidant in the presence of nitrogen oxides was proved by Gray and coworkers.¹¹

The maximum acidic environment is produced, which includes Hostavin N30. Regarding the structure of this additive that includes Cl and secondary amine, acidity will increase. By increasing of acidity, amine changes to salt and the role of stability is ruined, and degradation percentage will be increased.

Because of low secondary amine concentration in Chimassorb 2020 in comparison with Tinuvin 783, it causes less discoloration. Tinuvin 622 is the best additive (after Chimassorb 2020), because it is tertiary amine and decreases the discoloration of polymer. In some formulations, along with light stabilizers, antioxidants are used. Regarding to trend of changes in mechanical properties in Figures 2–4 show that Irganox HP 2225 is the best thermal stabilizer and after that Irganox B215 and Hostanox 03

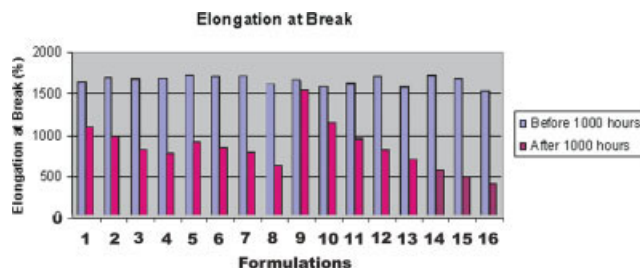


Figure 4 Comparison of elongation at break between compounds after and before 1000-h exposure. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

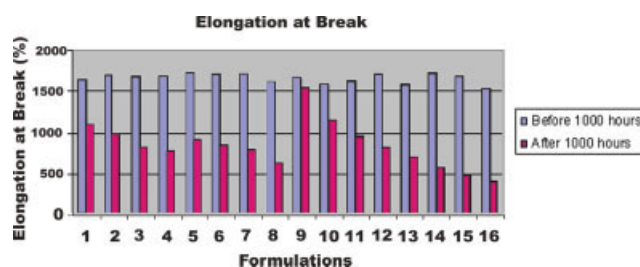


Figure 5 Comparison of yellowness index between compounds after and before 1000-h exposure. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

and after them the compounds without antioxidant are good. This is as a result of existing synergism relation between light and thermal stabilizers.

Irganox HP2225 is a mixture of 42.5% Irganox 1010, 42.5% Irgafos 168, and 15% lacton HP-136. Radicals from lactone are stable benzophoranonyl radicals, which cause great stability. Irganox B215 is a mixture of Irganox 1010 and Irgafos 168 with the ratio of 1 : 2. This additive is in the second level of selecting.

As shown in Figure 5, the polymer without antioxidant has the least discoloration.

CONCLUSIONS

In accordance with the results, the best formulation that response all the necessities for sample with the best physical mechanical properties is the formulation number nine. It means that 0.2% Tinuvin 783, 0.1% Irganox HP 2225, 0.1% Irgafos 168 and 0.1% Ca stearate are the best concentrations for PE rotational-molding grades.

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