

Study of Synergistic Effect of Light Stabilizer Additive, Conventional and Nanoparticles, Applied to Polyethylene Films Submitted to Ultraviolet Radiation

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Abstract Thermoplastic materials are sensitive to ultraviolet radiation (UV), which can cause structural changes, causing variation in mechanical properties and appearance. UV range between 250 and 400 nm is considered the most aggressive to polymers, and prolonged exposure to it results in breakage and/or crosslinking chains. Light stabilizer additives, blockers or absorbers are added to the polymers for protection in order to extend the life of the final product. The choice of the adequate light stabilizer additive system depends on factors such as resin final application, thickness, geographic location of exposure, presence of fillers in the composition, contact with chemicals, among others. This study evaluates different additive systems: conventional organic, inorganic nanotechnology base and the synergy between them when applied to polyethylene considering carbonyl index and UV/VIS results after aging by QUV chamber.

Keywords Polyethylene · Light stabilizer · UV · Nanoparticles · Ageing

Introduction

Aging is a term used in polymer science and engineering when properties of polymer change over a period of time. Changes can be detected on engineering properties as strength and toughness; physical characteristics as density; or

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chemical characteristics as aggressive chemical reactivity. These changes can be chemical or a result of interaction with the environment, for example when the oxidation leads to chain scission. Sometimes a series of aging-related phenomena occur simultaneously and/or in an interactive form [1]. The main purpose served by examining data on weathering of materials is to predict any potential changes of physical properties and appearance of those materials. Natural sunlight doesn't offer standard conditions: there are variations in clouds, smog, angle of the sun, rain, industrial environments, etc. Accelerated aging is used to guarantee the test is realized under standard methods [2].

Gulmine et al. studied degradation of polyethylene after artificial accelerated weathering. During degradation polar groups in the polyethylene are generated, as well as chain scission and cross-linking. As effects of these processes increase in crystallinity, density, hardness and surface cracking at late stages of degradation are observed [3]. Tavares et al. evaluated surface mechanical properties of polyethylene subjected to accelerated aging in Weathering Tester (QUV) and Weather-o-Meter (WOM) chambers. Modifications in nano mechanical properties were correlated to the corresponding chemical processes due to aging, which were measured through the carbonyl index profile obtained from ATR-FTIR [4].

Wang et al. [5] investigated mechanical properties of composites and the dispersion of the nanoparticles. The results have been shown that not only the tensile property but also the flexural modulus of the system have been evidently increased by the addition of calcium carbonate (NPCC).

The photodegradation of low density polyethylene (LDPE) containing nano particles of zinc oxide (nZnO) was analyzed by Yang and other [6] by FT-IR to monitor the development of oxidation products of films. Although the absorption of wavelengths below 350 nm by ZnO protect the polymer of photochemistry degradation, it can also induce heterogeneous photocatalytic oxidation of polymer.

Yang and other [7] studied the effect of UV radiation in LDPE films containing different concentrations of titanium dioxide nano particles (nTiO₂). When exposed on equipment for accelerated weathering test of type QUV, films resisted 400 h, although TiO₂ presence had promoted the exposition time reduction 50% in mechanical resistance due carbonyl groups formation. Liu and others studied blends of 80 wt% LLDPE and 20 wt% LDPE filled with nanoparticles of SiO₂ and TiO₂ at a ratio up to 5 wt%. The incorporation of nano-TiO₂ contributed to effectively improving the resistance to heating and ultraviolet irradiation of the composites [8].

This study have evaluated the additive systems hindered-amine light stabilizers (HALS), NPCC, nZnO and nTiO₂ and the synergy between them when applied to low density polyethylene (LDPE) considering carbonyl index and UV/VIS results after aging by QUV chamber. The samples were molded by cast film and aged in QUV 340 (ASTM G-154 - cycle 01) during until 3000 h, with intervals of 500 h. Tests of FT-IR, carbonyl index and UV/VIS comparing to the non-aged samples were performed to evaluate the performance of additive systems in relation to the degradation behavior of low density polyethylene.

Materials and Methods

Materials

Linear Low Density Polyethylene (LLDPE) butane-1 copolymer, narrow molar mass distribution, without slip additives, supplier Braskem, named ML 2400N, with melt index of 20.0 g/10 min and density of 0.926 g/cm³. This material was used as a vehicle for the masterbatches production.

Low Density Polyethylene (LDPE), supplier Westlake Chemical Corporation, named EN1817AA, with melt index of 1.7 g/10 min and density of 0.920 g/cm³, was used as a base resin for the films production.

Cyasorb UV-1164 is 2-[4, 6-Bis(2,4-dimethylphenyl)- 1,3,5-triazin-2-yl]-5-(octyloxy) phenol, produced by Cytec, whose physical form is represented by powder, with molecular weight 509. This material acts as a light stabilizer, offers high inherent UV stability and minimal color contribution.

Cyasorb UV-3529 is 1,6-Hexanediamine, N,N'-bis(2,2,6,6-tetramethyl-4-piperidinyl)-, Polymers with morpholine-2,4,6-trichloro-1,3,5-triazine, produced by Cytec, with physical form in pastilles and molecular weight 1690–1710. It acts as a light stabilizer, offers low volatility and selective reactivity.

Cyasorb UV-5411 is 2-(2'-Hydroxy-5'-octylphenyl)-benzotriazole, produced by Cytec, with physical form in powder and molecular weight 323. This material acts as a light stabilizer, offers minimal color contribution and strong absorption.

Cyasorb UV-531 is 2-Hydroxy-4-n-octoxybenzophenone, produced by Cytec, with physical form in powder and molecular weight 326. It acts as a light stabilizer, offers superb compatibility with polymers and other additives; shows cost efficiency.

Cyanox 2777 is 1:2 blend of 1,3,5-Tris(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione and tris (2,4-di-tert-butylphenyl) phosphite, produced by Cytec, with physical form in powder and melting point 166–171 °C. It is an antioxidant, offers minimal color and odor contribution; provides low volatility and very good processing stabilization; exhibits low gas yellowing and low water carry-over; shows compatibility with polymeric HALS and UVAs.

Nano calcium carbonate was provided by Nano Materials Technology Pte Ltd., represented in Brazil by Lagos Química, called NPCC-201, with specific density of 2.5 g/cm³, surface area of 40.0 m²/g and average particle size of 40 nm.

Nano titanium dioxide was supplied by Croda, named Atmer 7354, whose product is a concentrate of additive with 20.0% of active metal oxide content, compatible with polyolefin polymers.

Nano zinc oxide was provided by Croda, named Atmer 7355, whose product is a concentrate of additive with 30.0% of active metal oxide content, compatible with polyolefin polymers.

Preparation of Samples

For the study of the composites, proposed formulations were presented on Table 1, whose compositions were expressed as percentage, in weight.

Formulations were produced in single screw extruder, with screw's diameter of 25 mm and L/D = 30. The heat profile was 120/130/140 °C for feed, compression and dosage zones, respectively, and 140 °C on head. It was used screw rotation of 50 rpm.

To prepare film samples, a casting film extruder Killion/Davis, standard single screw, model KL125, was used with heat profile 120/130/150/155/160 °C, funnel to flat die, producing films with thickness 6 mils or 152 µm.

Analytical Methods

The accelerated aging was conducted in a test chamber UV condensation (QUV), Q-Lab—QUV/se, to simulate the effects of degradation on the surface of specimens, usually generated by exposure to sunlight, rain and dew. The specimens were exposed to radiation generated by UV-B lamp-340, with 8 h of UV cycle to 60 °C/irradiance 0.89 W/m² and condensation cycle of 4 h to 50 °C, repeating for 3000 h, with intervals each 500 h to perform analyses of carbonyl index and UV/VIS.

Analyses of Fourier Transform InfraRed (FT-IR) were carried out for verification of the polymer oxidation through the carbonyl index, according to ASTM D 5576, Digilab FTS7000e model, coupled with Universal ATR device ("Sampling Accessory"), in the range of 400–10,000 cm⁻¹ with resolution 2 cm⁻¹.

Ultraviolet visible spectrophotometry (UV/VIS) analyses were performed to determine the concentration of compounds that absorb radiation in that range and to verify how much light passes through a sample, using equipment Perkin Elmer, model Lambda 900, in the range of 280–700 nm.

Results

The results of the carbonyl index for the different compositions of samples studied were shown on Table 2.

It was possible to observe the effects of photodegradation on samples #4, #5 and #6 (nCaCO₃, nTiO₂ and nZnO, respectively) when compared with #13 (control). #13 sample was a conventional and simple formulation with antioxidant and light stabilizer, and then UV radiation was not so aggressive. It was observed nano

Table 1 Formulation of composites (% in weight)

Component/formula	#2	#3	#4	#5	#6	#7	#8	#9	#10	#11	#12	#13
HALS-3529						0.20	0.20	0.20	0.20	0.20	0.20	
UV-1164						0.10						0.30
UV-531	0.30						0.10					
UV-5411		0.30						0.10				
Nano CaCO ₃ -NPCC-530 (100%)			0.30						0.10			
Nano TiO ₂ -Atmer 7354 (20%)				1.50						0.50		
Nano ZnO-Atmer 7355 (30%)					1.00						0.33	
AO-2777	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06
LDPE	99.64	99.64	99.64	98.64	98.64	99.64	99.64	99.64	99.64	99.24	99.41	99.64

Table 2 Carbonyl Index (CI) of composites

Description	% 0 h	% Δ CI 500 h	% Δ CI 1000 h	% Δ CI 1500 h	% Δ CI 2000 h	% Δ CI 2500 h	% Δ CI 3000 h
#2: 0.3% UV-531	0.009	0.012	0.021	0.036	0.077	0.509	
#3: 03 94 UV-5411	0.009	0.054	0.460	1.236	1.797		
#4: Nano CaCO ₃ NPCC 530	0.021	1.555	5.090				
#5: Nano TiO ₂ —Atmer 7354 (20%)	0.022	1.775	5.879				
#6: Nano ZnO—Atmer 7355 (30%)	0.020	0.406	1.059	1.686	2.408		
#8: 02% HALS—3529 & 0.1% UV-531	0.008	0.009	0.012	0.017	0.020	0.019	
#9: 02% HALS—3529 & 0.1% UV-5411	0.011	-0.004	-0.001	0.003	0.005	0.005	
#10: 02% HALS-3529 & 0.1% Nano CaCO ₃ NPCC 530	0.012	0.002	0.002	0.005	0.008	0.007	
#11: 02% HALS -3529 & 0.5% Nano TiO ₂ — Atmer 7354	0.014	0.032	0.039	0.053	0.071	0.099	
#12: 02% HALS—3529 & 0.33% Nano ZnO —Atmer 7355	0.016	0.019	0.022	0.031	0.040	0.047	
#13: Control	0.011	0.287	1.159				

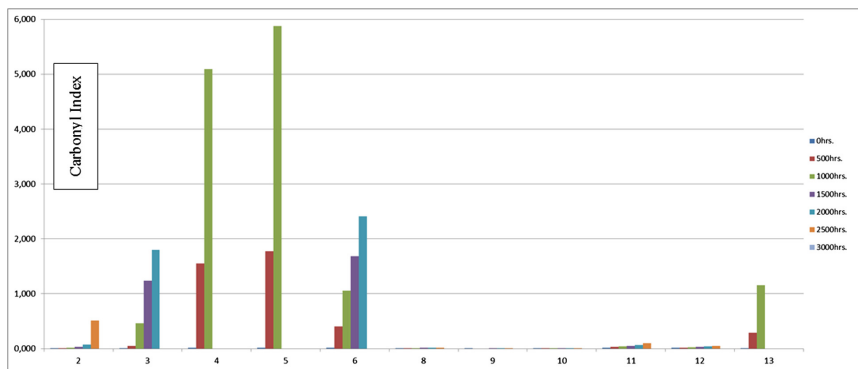


Fig. 1 Carbonyl index of composites, after ageing by QUV until 3000 h

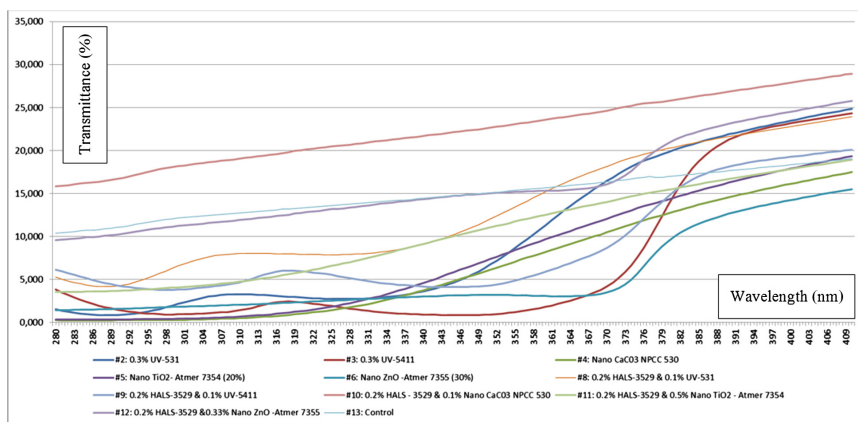


Fig. 2 Ultraviolet visible spectrophotometry (UV/VIS) of composites not aged

composites formulations showed increase in carbonyl index during ageing process. Despite these particles presented light stabilizing characteristic as barrier or blocking, they could generate free radicals, which accelerated the photodegradation process.

Formulations #9 and #10 (HALS 3529 + UV5411 and HALS 3529 + nCaCO₃) presented best results in carbonyl index, according to Fig. 1.

The results of ultraviolet visible spectrophotometry (UV/VIS) for composites of samples analyzed were exposed on Figs. 2, 3 and 4.

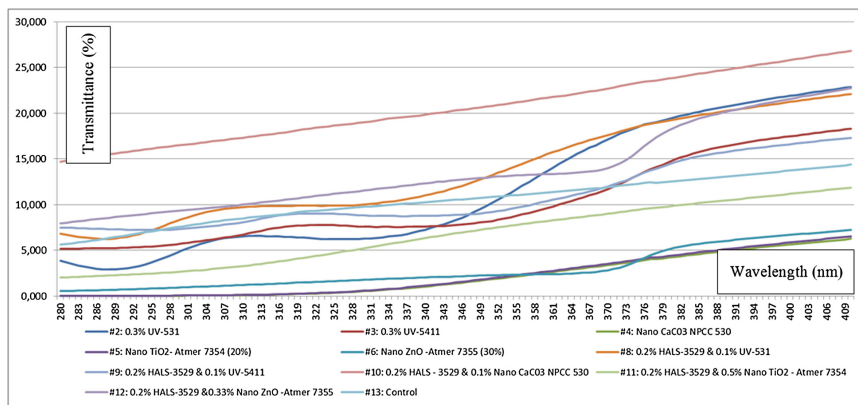


Fig. 3 Ultraviolet visible spectrophotometry (UV/VIS) of composites after 1000 h in QUV

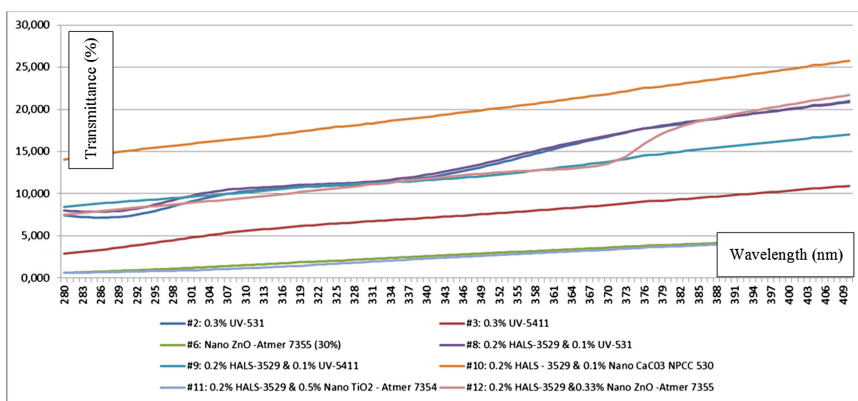


Fig. 4 Ultraviolet visible spectrophotometry (UV/VIS) of composites after 2000 h in QUV

Conclusion

In general, all systems of light stabilizer additives had a positive effect on the LDPE material, with different performances, according to the results showed.

As presented in figures above, it was possible to verify that organic additives (HALS) had its transmittance values increased after the aging period of the samples.

Despite the results of low formation of carbonyl, it was clear that the efficiency of organic additives decreased over time due to the migratory characteristic.

The balance between carbonyl index and UV/VIS showed formulations #10 (HALS 3529 + nCaCO₃) the best formulation light stabilizer, among the analyzed nanoparticle systems (nZnO, nTiO₂ and nCaCO₃, individually and/or in blend with HALS).

The advantage of nanoparticles, when compared to organic systems was that they didn't lose their efficiency over time by migration issues. However, it was important to know free radicals formation mechanisms, which interfered negatively in polymer protection as degradation by light exposure.

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References

1. White JR (2006) Polymer ageing: physics, chemistry or engineering? Time to reflect. *Chimie* 9:1396–1408
2. Massey LK (2007) *The effects of UV light and weather on plastics and elastomers*, 2nd edn. William Andrew Publishing, New York
3. Gulmine JV et al (2003) Degradation profile of polyethylene after artificial accelerated weathering. *Polym Degrad Stab* 79:385–397
4. Tavares AC et al (2003) The effect of accelerated aging on the surface mechanical properties of polyethylene. *Polym Degrad Stab* 81:367–373
5. Wang W et al (2007) Preparation and characterization of calcium carbonate/low-density-polyethylene nanocomposites. *J Appl Polym Sci* 106:1932–1938
6. Yang R et al (2010) Degradation products formed during UV exposure of polyethylene-ZnO nano-composites. *Polym Degrad Stab* 95(9):1533–1541
7. Yang R et al (2011) Spectroscopic studies of photodegradation of polyethylene films containing TiO₂ nanoparticles. *J Appl Polym Sci* 119(3):1330–1338
8. Liu G et al (2005) Effect of nanoscale SiO₂ and TiO₂ as the fillers on the mechanical properties and aging behavior of linear low-density polyethylene/low-density polyethylene blends. *J Polym Environ* 13(4):339–348