DEGRADATION BEHAVIOR OF LINEAR LOW DENSITY POLYETHYLENE BY ULTRAVIOLET RADIATION EXPOSITION FOR AGRICULTURAL APPLICATIONS

Patricia N. S. Poveda[1], Rosemeire Ciro[2], Hamilton M. Viana[3] and Leonardo G. A. Silva[4]

[1] Instituto de Pesquisas Energéticas e Nucleares (IPEN / CNEN - SP)
Av. Professor Lineu Prestes 2242
05508-000 São Paulo, SP
patricianegrini@usp.br

[2] Faculdades Oswaldo Cruz (FOC)
R. Brg. Galvão, 540-564 - Barra Funda
01151-0000 São Paulo, SP
rosemeireciro@msn.com

[3] Centro Universitário Fundação de Santo André (FSA)
FAENG
Av. Príncipe de Gales, 821 - Bairro Príncipe de Gales
09060-650 Santo André, SP
hmviana@gmail.com

[4] Instituto de Pesquisas Energéticas e Nucleares (IPEN / CNEN - SP)
Av. Professor Lineu Prestes 2242
05508-000 São Paulo, SP
lgasilva@ipen.br

ABSTRACT

Polyethylene is the most important polymer used in agricultural applications. Polymers are susceptible to changes in their chemical structures that affect their mechanical properties under weather condition. In Polyethylene, photo-oxidation can occur because of impurities or chromophore groups (catalytic residue, mineral fillers, some commercial additives as stabilizers, lubricants, plasticizers, etc.). The critical ageing factors for greenhouse built with LDPE film are: total solar radiation, air temperature, relative humidity, mechanical stress, agrochemicals, air pollution, and combinations of these factors. Exposure of plastics to UV radiation causes a loss in their mechanical properties and/or change in appearance, including reduced ductility, color changes, yellowing and cracking. Additives are added to plastics to enhance the durability of the final product. Today, there are several additive systems (light stabilizers) developed to work according to resin, final application, type of cultivation, and other characteristics. The main types of light stabilizers are: UV absorbers, quenchers and free radicals scavengers. In addition to the conventional organic additives, some inorganic additives were obtained recently with the development of nanotechnology. This study evaluates the different additive systems (HALS, NPCC, nZnO and nTiO$_2$), applied 0.25% (in weight) in LLDPE. The samples were mixed by high rotation homogenizer and extrusion. Later, the samples were molded by injection and aged in QUV-B simulating 6 months of exposure to weather. Tests of FT-IR and tensile strength comparing to the non-aged samples were carried out in order to evaluate the performance of several additive systems concerning the degradation behavior of linear low density polyethylene.

1. INTRODUCTION

Aging is a term used for many branches of polymer science and engineering, when the properties of polymer change over a period of time. The changes can be observed on engineering properties as strength and toughness; physical characteristics as density; or chemical characteristics as aggressive chemical reactivity. The origins of these changes can be chemical or a result of interaction with the environment, such as when the oxidation leads to chain scission. Sometimes a series of aging-related phenomena occur simultaneously and or interactive form [1].

The mainly purpose served by examining data on weathering of materials is to predict any potential changes of physical properties and appearance of those materials. Data on the aging behavior of plastics are acquired through accelerated tests and weather exposure. Natural sunlight is not standard; there are variations in clouds, smog, angle of the sun, rain, industrial environments, etc. So, is used to work with accelerated aging, under standard methods [2].

UV wavelengths from sunlight are an important component in outdoor degradation. The energy from sunlight is mainly visible light (700-400nm), infrared (manifested as heat), and UV light (400-10nm). Although UV radiation amounts to only 3% of the total radiation that reaches the earth, it is energetic enough to cause chemical reactions, weathering of polymers, and fading of certain dyes. The solar UV radiation spectrum is divided into three ranges. UV-A is the energy with wavelengths between 400 and 315nm. UV-B is the spectrum from 315 to 290nm. UV-C includes solar radiation below 290nm. Polyethylene films exposed to solar UV-B radiation readily lose their tensile strength as well as their average molecular weight [2].

Salem, Faouk and Kashif[3] studied films of low density polyethylene (LDPE) non-stabilized against formulations containing stabilizer type Hindered Amine Light Stabilizer (HALS) after exposure to ultraviolet radiation. Chemical-physical changes over the photo-oxidation process were investigated by tensile strength tests, infrared spectrophotometry (FT-IR) and thermal analysis (DSC). The results showed the use of stabilizer HALS was effective to keeping mechanicals properties of LDPE films after UV exposition. It was also observed that the rate of formation of carbonyl groups depends of time of UV exposure, as well as the polymer crystallinity is strongly influenced by UV radiation and presence of HALS [4].

Deschmane, Yun and Misra [5] investigated the effect of calcium carbonate in mechanical properties of high density polyethylene (HDPE) compounds. The characteristic of reinforcement was evidenced through the results of impact resistance where the fracture characteristics were attributed mainly to the effect nucleante promoted by the presence of calcium carbonate, decreasing the size of the espherulites [6]. Have not been reported studies of the effect of nano calcium carbonate on the properties after aging (natural or artificial).

Photodegradation of LDPE containing nano particles of ZnO was analyzed by Yang et al [7] by FT-IR to monitor the development of oxidation products of films. Although the absorption of wavelengths below 350nm by ZnO protect the polymer of photochemistry degradation, can induce heterogeneous photocatalytic oxidation of polymer. The behavior degradation of LDPE film was compared to compounds containing 0.25% and 0.75% of ZnO and these results were compared with similar films obtained by nano particles of TiO_2. When subjected to UV radiation, the films with additive ZnO accelerated the formation of carbonyl groups

and the CO_2 production; however, the TiO_2 films had an even faster development in the formation of carbonyl groups. Apparently, the reduction of mechanical properties are more related to the carbonyl groups than the generation of CO_2 [8].

Yang et al. [9] studied the effect of UV radiation in LDPE films containing different concentrations of nano particles of TiO_2. Films presented absorbance of UV wavelengths up to about 350nm, retaining good transmission in the visible range and clarity optic. When exposed on equipment for accelerated weathering test of type QUV, films resisted 400h, although TiO_2 presence had promoted the exposition time reduction 50% in mechanical resistance due carbonyl groups formation.

Films prepared with PE/TiO_2 compounds were investigated by Zhao et al. [10], in order to verify the photocatalytic degradation after exposure to ultraviolet light and sunlight. The results indicated that the process of photocatalytic degradation of PE/TiO_2 films was faster and more complete than the simple photolysis of pure PE film under UV radiation and sunlight. The main products of degradation of PE/TiO_2 films are CO_2 and H_2O. Different levels of TiO_2 nano particles promote different degradation rates.

This study evaluates the additive systems (HALS, NPCC, nZnO and $nTiO_2$), applied 0.25% (in weight) in LLDPE. The samples were mixed by high rotation homogenizer and, further, extrusion. Later, the samples were molded by injection and aged in QUV-B simulating 6 months of exposure to weather. Tests of FT-IR, carbonyl index and tensile strength comparing to the non-aged samples were analyzed to evaluate the performance of additive systems in relation to the degradation behavior of linear low density polyethylene.

2. EXPERIMENTAL

2.1. 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/10min and density of 0.926 g/cm^3. This material was used as a vehicle for the production of masterbatches and obtaining specimens injected.

Tinuvin 783 is a mix 1:1 of Hindered Amine Light Stabilizer (HALS) with low molar mass (Chimassorb 944), and high molar mass (Tinuvin 622). This additive is produced by BASF and used as standard UV stabilizer, whose physical form is represented by slightly yellowish granules or tablets, with density 514 g/l and fusion of 55°C to 140°C.

The 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/cm^3, surface area of 40.0 m^2/g and average particle size of 40nm.

The nano titanium dioxide was supplied by Croda, named Atmer 7354, whose product is a concentrate of additive with 20% of active metal oxide content, compatible with polyolefin polymers.

The nano zinc oxide was provided by Croda, named Atmer 7355, whose product is a concentrate of additive with 30% of active metal oxide content, compatible with polyolefin polymers.

2.2. Preparation of samples

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

Table 1 – Samples' formulations (%, in weight).

Formulation	Description	LLDPE	Nano CaCO$_3$	Nano TiO$_2$	Nano ZnO	UV Additive
PE100	Polyethylene	100.00	0	0	0	0
PECa25	NPCC Additive	99.75	0.25	0	0	0
PETi25	nTiO$_2$ Additive	99.75	0	0.25	0	0
PEZn25	nZnO Additive	99.75	0	0	0.25	0
PEUV25	HALS Additive	99.75	0	0	0	0.25

The formulations that contained nano calcium carbonate and the ultraviolet stabilizer additive default, have been prepared initially by mixing in high rotation homogenizer for better dispersion of components, forming a concentrated (masterbatch). Then, pellets were formed by extrusion, and later, inject specimens. Samples of nano titanium dioxide and nano zinc oxide were provided as concentrated in polyethylene, therefore, were only applied to thermoplastic resin in appropriate proportion, and after, obtain injected specimens.

Components of formulations were weighed in balance Marte, model AS 5500, with capacity of 5000g.

Formulations were prepared in high rotation homogenizer MH, model MH-600, capacity of 500g. The components of formulations were introduced at the same time in equipment and the mix occurred by shear, with velocity of 3600 rotations per minute (rpm).

The molten material was ground into mill BGM, leading to reduced pieces and dosage of these in mono screw extruder.

Formulations were produced in mono screw extruder BGM, model EL-25, with screw diameter of 25mm and L/D 30. The heat profile was 110/120/130°C for feed, compression and dosage zones, respectively, and 140°C on head. It was used screw rotation of 50rpm.

To prepare injected samples, was used injector Arburg, model Allrounder 270S 400-100, with heat profile 120/130/150/155/160°C, funnel to nozzle.

2.3. Analytical methods

The accelerated aging was conducted in a test chamber UV condensation (QUV) 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-310, with 8h of UV cycle to 70°C and condensation cycle of 4h to 50°C, repeating for 172 hours, simulating natural exposure of 06 months.

The mechanical tests were carried out to evaluate the resistance of nano composites through properties at break, elongation at break and the secant module. The analyses were performed per ASTM D-638, in Zwick universal testing machine; model Z030, with speed of 50 mm/min and processing of data through Software Test Xpert Machine V.6.01.

Analyses of Fourrier Transform InfraRed (FT-IR) were carried out for verification of the oxidation of the polymer through the carbonyl index, according to ASTM D 5576, Perkin Elmer, spectrometer Spectrun One model, coupled with Universal ATR device ("Sampling Acessory"), in the range of 400 to $10000 cm^{-1}$ with resolution $2 cm^{-1}$.

2.4. Results

The results of the measurements of mechanicals properties for the different compositions of samples studied are shown in Table 2.

Is possible to observe the effects of photodegradation on sample PE100 when compared with PE100 STD. PE100 not contain additive, then UV radiation is very aggressive, caused the decline of the properties (decrease of 45.5% in tensile modulus, 27.8% in yield strength and breaking of the sample while the PE100 STD did not break after stretching).

Considering PE100 the reference for sample post ageing, the nanoparticles presented increase in tensile modulus (55.5% to PECa25, 53,6% to PETi25 e 38,8% to PEZn25). These results showed that nanoparticles have given greater stiffness to the polymer. Due to this characteristic, it has greater tensile strength in breaking and lower elongation at break.

Despite the lower results in modulus of elasticity and strength resistance, it was verified that the sample PEUV25 had more deformation and not broke in the same test condition.

Table 2 - Results with polyolefin polymers after accelerated aging by QUV-B.

Sample	Tensile Modulus E (MPa)	Yield Strength (MPa)	Yield Elongation (%)	Breaking Strength (MPa)	Breaking Elongation (%)
PE100 STD*	188.80 ± 20.49	10.72 ± 0.11	38.01 ± 1.40	-	-
PE100**	103.00 ± 6.04	7.74 ± 0.19	61.65 ± 28.24	5.90 ± 1.47	173.47 ± 33.77
PECa25**	160.20 ± 15.11	10.79 ± 0.07	43.03 ± 0.99	9.34 ± 0.68	135.91 ± 8.65
PETi25**	158.20 ± 14.10	10.11 ± 0.06	42.47 ± 0.99	8.47 ± 0.79	131.80 ± 14.77
PEZn25**	143.00 ± 17.00	10.30 ± 0.04	72.68 ± 26.29	7.76 ± 0.78	152.17 ± 12.21
PEUV25**	79.00 ± 2.12	7.44 ± 0.09	96.97 ± 3.83	-	-

* reference sample, standard material, not aged.

** sample post ageing by chamber QUV-B.
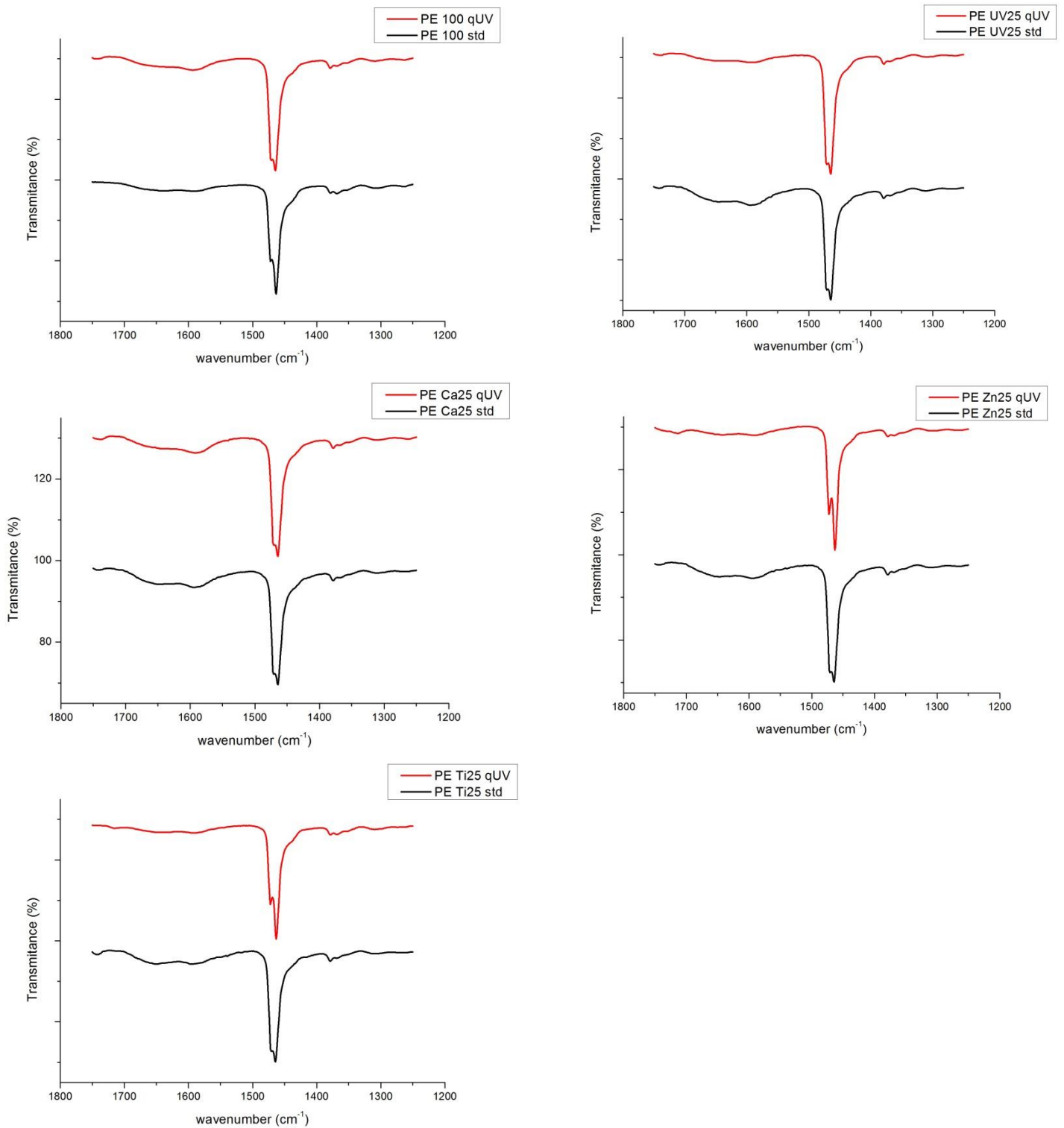
- no break.

Figure 1 shows FTIR spectra of all samples.
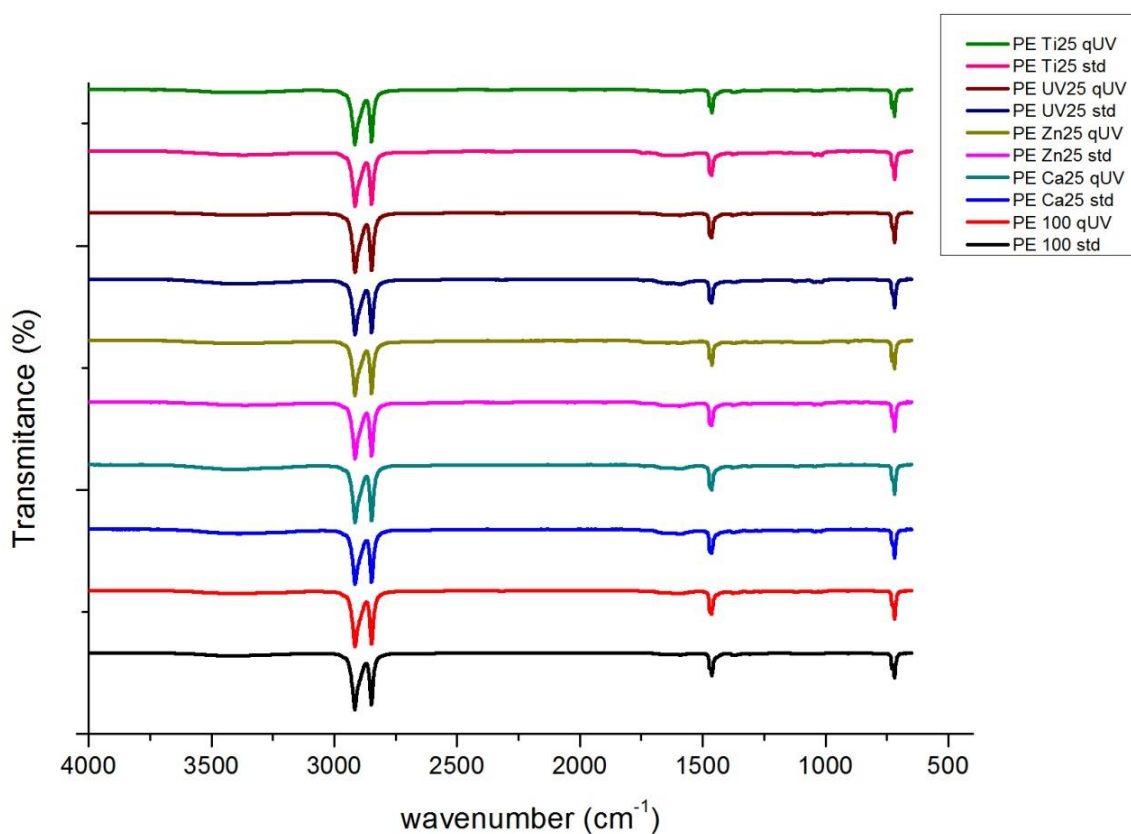
Figure 1: FTIR spectra of all samples without (*.std) and with (*.qUV) UV ageing.

Figure 2 illustrates FTIR spectra, additivation, sample aged and not aged.

Figure 2: FTIR spectra, by additivation without (*.std) and with (*.qUV) UV ageing.

The carbonyl index is calculated as the ratio of the intensity of the carbonyl band (1710-1730 cm^{-1}) in the FTIR spectrum and the intensity of the chosen reference band in the material examined [11, 12]. In the case of Polyethylene, the band was chosen to group C-H stretching (1300-1400 cm^{-1}). Table 3 shows the values obtained and indicates that the carbonyl index suffers reduction after aging for all samples. The most effective additive on reduction of carbonyl index is the HALS, followed by nZnO, nTiO$_2$ and the nCaCO$_3$. Standard polyethylene presented superior carbonyl index.

Table 3 - Heights of the carbonyl stretching bands and C-H stretch.

Sample	$h_{C=O}$ (1715 cm^{-1})	h_{C-H} (1300-1400 cm^{-1})	Carbonyl index ($h_{C=O}$ / h_{C-H})	CI$_{quv}$ / CI$_{std}$
PE Ca25 QUV	0.019	0.149	0.128	88.1%
PE Ca25 STD	0.021	0.145	0.145	
PE Ti25 QUV	0.011	0.140	0.079	77.5%
PE Ti25 STD	0.014	0.138	0.101	
PE UV25 QUV	0.009	0.151	0.060	41.2%
PE UV25 STD	0.020	0.138	0.145	
PE Zn25 QUV	0.007	0.144	0.049	44.7%
PE Zn25 STD	0.015	0.138	0.109	
PE 100 QUV	0.014	0.143	0.098	183.2%
PE 100 STD	0.007	0.131	0.053	

STD reference sample, not aged.
QUV sample post ageing by chamber QUV-B.

3. CONCLUSIONS

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

The sample based HALS had a mechanical result (yield strength) close to the sample of LLDPE without additives (aging), however, the sample not broke in tensile strength. The polymer with HALS additive (PEUV25) was more tenacious because, probably, this additive didn't interfere on crystallinity or its influence was minimum. It had presented the carbonyl index lowest among all the studied systems.

Nanoparticle-based samples, as well as reduce the carbonyl index, showed an increase of mechanical properties. These results can be explained due to the physical characteristics of these materials, which can act as nucleante for the polyethylene, conferring mechanical reinforcement and turn the polymer more stiffness.

The balance between carbonyl and mechanical properties index showed nZnO the best formulation light stabilizer, among the analyzed nanoparticle systems (nZnO, nTiO$_2$ and nCaCO$_3$).

Thus, it was concluded that the best UV additives systems evaluated were based on HALS (PEUV25), keeping the tenacity of the polymer and, nZnO (PEZn25), offering greater stiffness to polymer.

ACKNOWLEDGMENTS

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