

Avaliação do efeito do tratamento corona na performance de estabilizadores de UV em filmes de PEBD

Evaluation of effect of corona treatment on the performance of UV stabilizers in LDPE films

Glaucea Warmeling Duarte¹, Camila Machado de Oliveira¹,
Luciano da Silva¹, Alexandre Gonçalves Dal Bó¹,
Márcio Antônio Fiori²

¹ Programa de Pós Graduação em Ciência e Engenharia de Materiais, Universidade do Extremo Sul Catarinense, UNESC, CEP: 88806-000, Criciúma, Santa Catarina, Brasil.

² Programa de Pós Graduação em Ciências Ambientais e Programa de Pós Graduação em Tecnologia e Gestão da Inovação. Universidade Comunitária da Região de Chapecó, UNOCHAPECÓ, CEP: 89809-000, Chapecó, Santa Catarina, Brasil.

e-mail: gwduarte@gmail.com, luciano.silva@unesc.net, adalbo@unesc.net, marciofiori@gmail.com.

RESUMO

A indústria de polímeros tem passado por muitos avanços na última década, dentre eles, podem-se citar as inovações em processamento e no uso de aditivos, o que permite que eles sejam utilizados em diversas aplicações, especialmente quando expostos ao ambiente externo. Porém, para algumas aplicações específicas, o polímero precisa ser submetido a tratamentos de superfície, com o objetivo de aumentar a rugosidade superficial. Por este motivo, muito ainda precisa ser estudado no que diz respeito aos aditivos utilizados no processamento de polímeros quando ele é submetido a processos de transformação, podendo-se citar o tratamento corona. Desta forma, este trabalho tem o objetivo de avaliar as modificações estruturais causadas em aditivos estabilizantes presentes em filmes poliméricos quando são submetidos a tratamento corona. Três diferentes absorvedores de UV foram avaliados: benzofenona, benzotriazol e triazina. Os filmes foram processados por *spin coating* e submetidos à radiação ultravioleta, com o objetivo de simular a exposição externa do polímero e a tratamento corona. Analisando os resultados obtidos, pode-se perceber que o único aditivo que resistiu às condições de tratamento foi o benzotriazol, mantendo a absorção da radiação ultravioleta, mesmo após o tratamento corona e protegendo o polímero da degradação UV. Os outros aditivos sofreram processos degradativos, causadas pelo tratamento corona, e a absorção da radiação ultravioleta, apresentada previamente, deixa de existir.

Palavras-chave: Aditivo. Tratamento Corona. Filme Polimérico. Estabilizante. Radiação UV.

ABSTRACT

The polymer industry has undergone many advances in the last decade, among them, innovations in the processing and in the use of additives, which enable the use of polymers in several areas, especially, when exposed to external environment. However, for some specific applications, the polymer must be submitted to surface treatments in order to increase its superficial roughness. Then, much remains to be studied regarding the behavior of these additives when exposed to transformation processes in which the polymers are normally subjected, as for example, the corona treatment. Thus, this study aims to evaluate the structural modifications in stabilizing additives present in polymeric films, when subjected to corona treatment. Three different UV absorbers additives were evaluated: benzophenone, benzotriazole and triazine. The films were processed by spin coating and subjected to ultraviolet radiation, in order to simulate the external exposition of the polymer, and corona treatment. Analyzing the results obtained, it was realized that the only additive that resisted to the treatment conditions was benzotriazole, maintaining the absorption of ultraviolet radiation even after corona treatment and protecting the polymer from UV degradation. The other additives suffered degradation pro-

cesses, caused by corona treatment, and the absorption of ultraviolet radiation presented earlier, ceases to exist.

Keywords: Additives. Corona Treatment. Polymeric Films. Stabilizers. UV radiation.

1. INTRODUCTION

Polyolefins, such as polypropylene and polyethylene, are normally chemically inert, nonporous and with low surface tension (0,031 N/m e 0,032 N/m, for PE e PP, respectively)[1], due to its nonpolar characteristics. In the packaging industry, the surface tension is important to determine if a substrate may or may not be adhered to the polymer [2]. In general, the polymer must have a surface tension about 0,010 N/m a 0,020 N/m higher than the substrate which will interact with [1].

Therefore, these materials are constantly submitted to surface treatment techniques to modify its surface properties. The surface treatments change the surface properties through chemical reactions or by altering the surface morphology (increasing the roughness), increasing the surface tension and favoring the interaction with other substances as, for example, solvents, coatings, paints, other polymers, etc. [1,3].

The most applied technique used to change the polymer surface is the corona treatment. It is a surface modification technology frequently used by the packaging industry for increasing surface tension and polarity of films in order to improve printability, wettability and adhesion properties [12].

This technique consists of an electrical discharge, in atmospheric air, which ionizes the oxygen, nitrogen and other gases presented in the air. The ions, or activated species of oxygen react to produce ozone, a powerful oxidizing agent. The energy of the particles (1-20 eV) are sufficient to break C-C and C-H bending (2,54 eV and 3,79 eV, respectively) and generate free radicals on the polymer surface, which can react with oxygen atoms and form polar groups as, for example, alcohol (C-OH), ketones (C=O), ethers (C-O), etc.[1, 4].

Besides, polymeric materials exposed to external environment are submitted to ultraviolet radiation, warm, humidity, atmosphere contaminants, oxygen and others. These factors may initiate degradative process in polymers, causing many chemical reactions and resulting on the deterioration of properties. So, control or limit these reactions is an efficient way to increase the useful life of polymers [5]. Many kinds of degradation process are known. Although, the most important one is the oxidation, that can be initiated by different factors as, for example, ultraviolet radiation [6], known as photodegradation [7].

The photodegradation of plastics exposed to solar radiation is considered the most destructive kind of degradation of their properties, which takes place under the influence of UV-A radiation (315–400 nm), leading to scission and cross-linking reactions and oxidation. Photodegradation products are often the carbonyls (C = O), hydroxyl (OH) groups, and the vinyl groups [13]. The ultraviolet radiation corresponds to about 5% of the ultraviolet radiation [8]. Part of this radiation is filtered by the ozone layer, so that the shorter wavelength that reaches earth is about 290 nm [9].

The use of polymeric materials in external environment is only possible due to the use of additives which minimize its degradation by photochemical reactions, known as UV stabilizers [10, 11]. UV-stabilisers are added to plastic films to increase their durability, by reducing oxidation reactions. UV absorbers, stabilisers HALS (hindered amine light stabilisers) and nickel based stabilisers (nickel quenchers) belong to the general category of UV stabilisers [13]

One example of industry which use this kind of additives is the packaging industries. However, the process used in the manufacture of these films employs the corona treatment directly on the production line, exposing not only the films, but also the additives, to the degradative effects of ozone generated. So that, it is necessary to evaluate the effect of this treatment on the structure and function of stabilizing additives.

The present work aims to evaluate the possible interaction or reaction resulting from exposure of polymeric films stabilized with anti-UV additives to corona treatment and, also, verify the changes caused by this corona treatment on the efficiency of these additive when posteriorly exposed to UV radiation.

2. MATERIALS AND METHODS

The additives used in this work are UV absorbers, which were purchased from Sigma Aldrich and have the molecular structure showed in Figure 01. The polymer used was LDPE (low density polyethylene), purchased from Braskem (TN7006). This polymer has no additives included on its composition, which facilitates the analyses of the additives evaluated. The solvents used were purchased from different providers and used

without any purification.

The films of LDPE containing the additives showed in Figure 01 which were processed used the spin coating technique using hexane as solvent. As LDPE is insoluble at room temperature, the solutions containing the polymer and the additive were heated until 100 °C under continuous stirring before being spin coated. All the films have the same thickness.

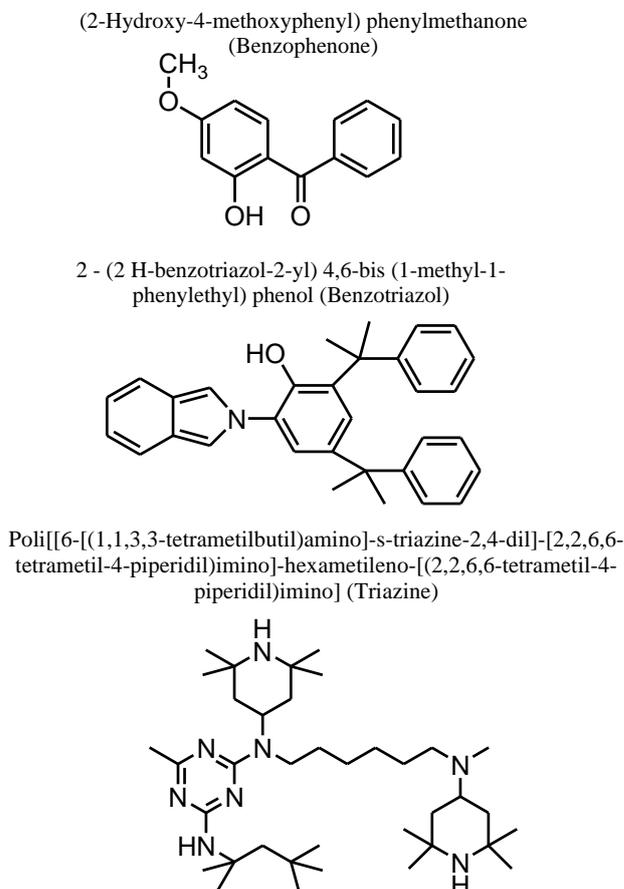


Figura 1: Molecular structure of the additives used.

The samples obtained were submitted to three different steps of superficial treatment: (1) exposition to UV-C radiation during 7 days, (2) exposition to corona treatment until a superficial tension of 36 dynes and (3) after corona treatment, the samples were submitted to UV radiation one more, to verify the maintenance of anti-UV characteristics. The UV treatment used UV-C lamp with wavelength of 253.7 nm in a higher incidence. The UV chamber and the corona treatment station are shown in Figure 02.

After superficial treatments, the samples were characterized by Fourier transform infrared spectroscopy (FT-IR), ultraviolet-visible spectroscopy (UV-vis) and thermogravimetric analysis. The IR spectra of the samples obtained were recorded with Fourier Transform Infrared Spectrophotometer IRPrestige-21 (SHIMADZU) within the wavenumber range of 700 – 4000 cm^{-1} . The UV-vis analysis was recorded in a UV-1800 (SHIMADZU), with scan range of 200-400 nm and deuterium lamp.



Figure 2: (a,b) UV chamber; (c) Corona Treatment Station.

3. RESULTS AND DISCUSSION

Figure 03 shows the FT-IR spectrum for all the molecule analyzed in this work: (A) low density polyethylene (LDPE), (B) (2-Hydroxy-4-methoxyphenyl) phenylmethanone (Benzophenone), (C) 2 - (2 H-benzotriazol-2-yl) 4,6-bis (1-methyl-1-phenylethyl) phenol (Benzotriazol) and (D) Poli((6-((1,1,3,3-tetrametilbutil)amino)-s-triazine-2,4-dil)-(2,2,6,6-tetrametil-4-piperidil)imino)-hexametileno-((2,2,6,6-tetrametil-4-piperidil)imino) (Triazine). The characteristic bands for each molecule are described below:

- A. 2919 cm^{-1} , 2845 cm^{-1} , 1459 cm^{-1} and 720 cm^{-1} are related to the different vibration mode of C-H bending.
- B. 3395 cm^{-1} – phenol O-H bending; 3057 cm^{-1} – C-H bending in aromatic compounds; 2980 cm^{-1} – C-H in aliphatic compounds; 1633 e 1693 cm^{-1} – C=O bending; and 1259 cm^{-1} – C-O-C bending.
- C. 3440 cm^{-1} – O-H bending in phenolic groups; 3045 cm^{-1} – C-H bending in aromatic compounds; 2956 and 2865 cm^{-1} – C-H bending in aliphatic groups; 1590 cm^{-1} – C=N bending; and 1436 cm^{-1} – C-O bending.
- D. 3445 cm^{-1} – N-H bending in amines; 2928 cm^{-1} e 2860 cm^{-1} – C-H bending in aliphatic groups; and 1545 cm^{-1} – C=N bending.

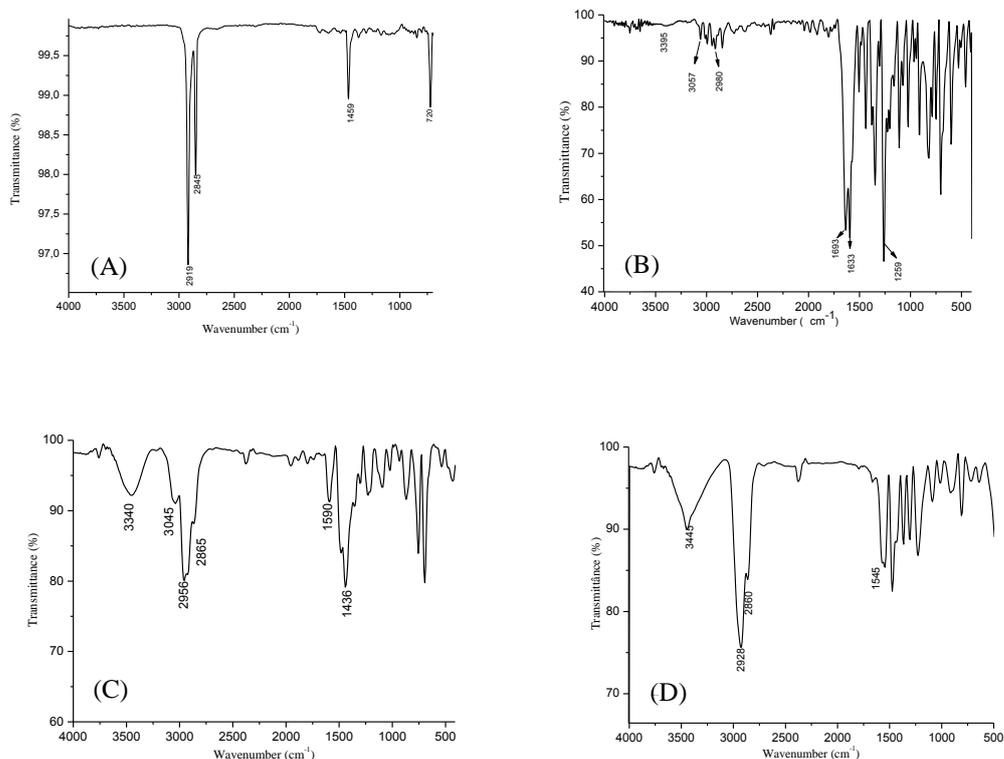

Figure 3: FT-IR spectrum for the molecules analyzed. (A) LDPE, (B) Benzophenone, (C) Benzotriazol and (D) Triazine.

Figure 04 shows the UV-vis analysis for all the absorbing molecules analyzed and the linearity relation between absorbance and the concentration of these molecules solubilized in dichloromethane. The linearity condition guarantees that all the experiments follow the Beer-Lambert law (equation 01), in the range of concentrations studied.

$$A = \epsilon cl \tag{1}$$

The Figure 04(A) shows that LDPE does not absorb ultraviolet radiation. Benzophenone (Figure 04(B)) and Benzotriazol (Figure 04(C)) show similar absorption spectra. Both molecules absorb in regions of high, medium and low values of ultraviolet wavenumber. On the other hand, Triazine (Figure 04(D)) show a spectra with significant absorption in low ultraviolet wavenumber.

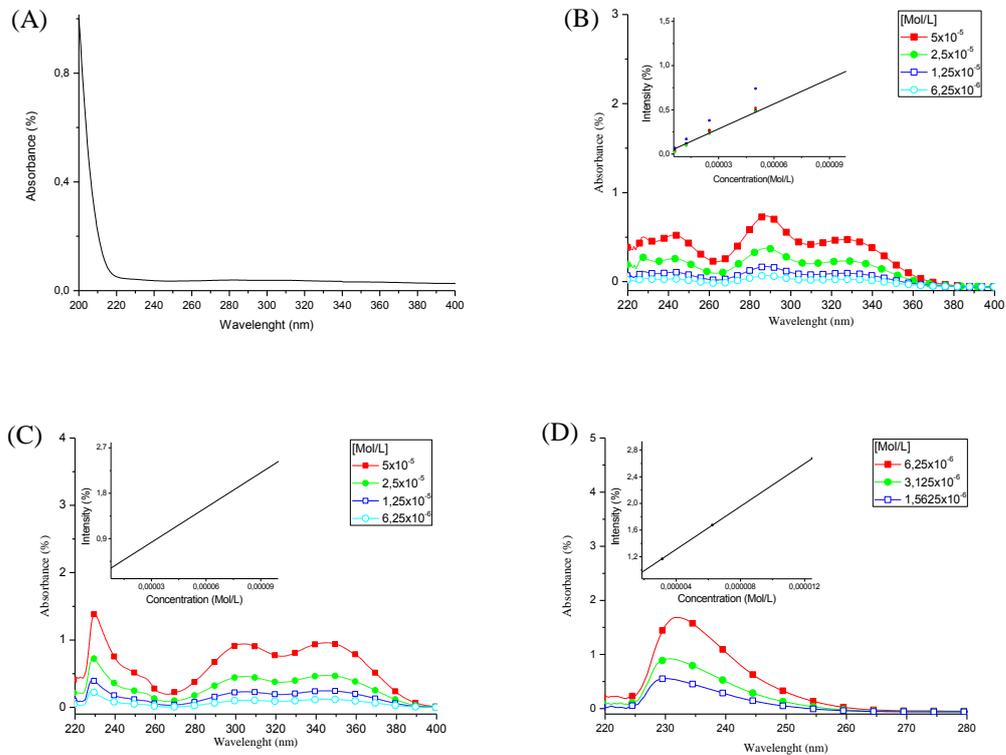


Figure 4: UV-vis spectrum with added linearity curve for absorbance versus concentration for the molecules analyzed. (A) LDPE Pure (B) Benzophenone, (C) Benzotriazol and (D) Triazine.

By equation 01 and the results obtained in the UV-vis spectra, it is possible to determine de molar absorptivity for each molecule: Benzophenone: $1,52 \times 10^4 \text{ L.mol}^{-1}.\text{cm}^{-1}$; Benzotriazol: $2,84 \times 10^4 \text{ L.mol}^{-1}.\text{cm}^{-1}$ and Triazine: $2,12 \times 10^5 \text{ L.mol}^{-1}.\text{cm}^{-1}$.

The results indicate benzophenone shows the lower value of molar absorptivity, followed by benzotriazol and triazine. Therefore, it is possible to conclude triazine is the additive which can be used in minor amount when compared to the other additives. Although, benzophenone and benzotriazol are the molecules with ability to absorb ultraviolet radiation in all UV spectra (UV-A, UV-B e UV-C). Between these two additives, the benzotriazol has the higher molar absorptivity.

Figures 05 and 06 show the FT-IR and UV-vis spectra for LDPE submitted to UV radiation and corona treatment. The samples exposed to UV radiation and corona treatment showed differences in the bending formed. For both samples, there was the formation of C=O bending in about 1728 cm^{-1} . Although in the sample treated with ultraviolet radiation, there was the formation of peak related to C-O bending in 1039 and 992 cm^{-1} , what does not happen with the sample submitted to corona treatment.

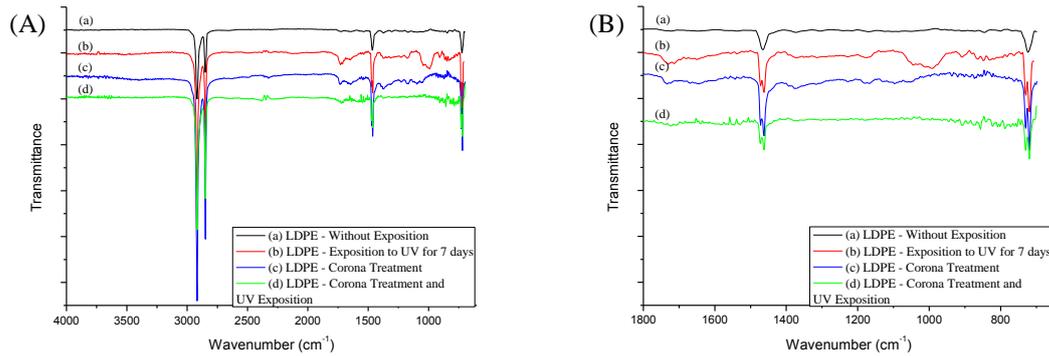


Figure 5: FT-IR spectrum for LDPE. Comparison between the samples without exposition, submitted to UV radiation for 7 days, submitted to corona treatment and submitted to corona treatment with posterior exposition to UV radiation. (A) Complete FT-IR spectrum; (B) Approximation of the FT-IR spectrum between 1800 cm^{-1} and 650 cm^{-1} .

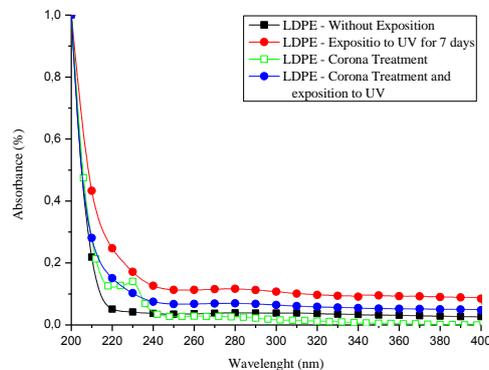


Figure 6: UV-vis spectrum for LDPE. Comparison between the samples without exposition, submitted to UV radiation for 7 days, submitted to corona treatment and submitted to corona treatment with posterior exposition to UV radiation.

The UV-vis analysis showed that with corona treatment there was the formation of an absorption peak at about 230 nm, proving the formation of C=O bending, that does not exist in the samples without treatment. For the samples submitted to UV radiation, before or after corona treatment, there was no evidence about the formation of new absorption peaks. Although there was an increase in the absorbance intensity in all the spectrum (200 – 400 nm), suppressing like that the peak that should exist in 230 nm due to the oxidation of the polymeric chain.

Figures 07 and 08 show the FT-IR and UV-vis spectra for the sample containing 99% of LDPE and 1% of benzophenone. By the FT-IR analysis it can be observed there was no modification in the chemical structure of the polymer or the additive in the bendings with vibration mode in the spectrum region above 1800 cm^{-1} , although there was a decrease in the intensity of the peaks presented below 1800 cm^{-1} . In 1375 cm^{-1} there was the formation of C-O bending in all the samples submitted to the three kind of superficial treatments. This is an indicative of the degradation of the additive, which is more preminent for the samples submitted to UV radiation.

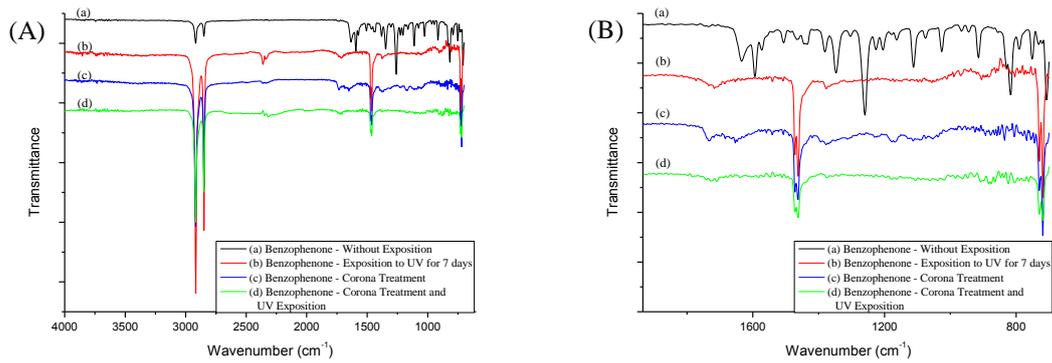


Figure 7: FT-IR spectrum for the sample with 99% of LDPE and 1% of benzophenone. Comparison between the samples without exposition, submitted to UV radiation for 7 days, submitted to corona treatment and submitted to corona treatment with posterior exposition to UV radiation. (A) Complete FT-IR spectrum; (B) Approximation of the FT-IR spectrum between 1800 cm^{-1} and 650 cm^{-1} .

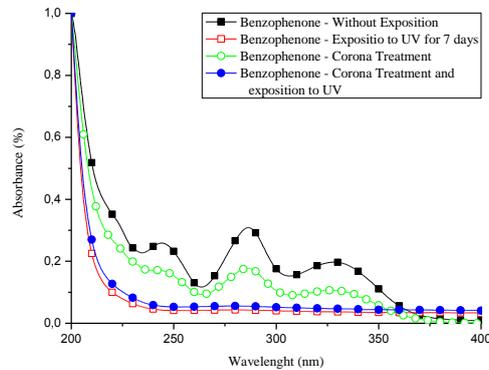


Figure 8: UV-vis spectrum for the sample with 99% of LDPE and 1% of benzophenone. Comparison between the samples without exposition, submitted to UV radiation for 7 days, submitted to corona treatment and submitted to corona treatment with posterior exposition to UV radiation.

By the UV-vis spectra it is possible to notice that corona treatment promotes a decrease in the sample absorbance, what supports the FT-IR results. For the samples exposed to UV radiation, there was an absence of absorbance peaks, indicating the degradation or consumption of the additive. The peaks related to the formation of C=O, resulting from photodegradative reaction in the polymer, does not appear in the UV curves because it may be suppressed by the already existing absorption bands in 230 nm.

Figures 09 and 10 show the FT-IR and UV-vis spectra for the sample containing 99% of LDPE and 1% of benzotriazol. By the analysis of FT-IR it is noticed that sample submitted to corona treatment presented more changes in its structure. Comparing the spectra of Figure 09(B) and 09(C) it is noticed that occurred a decrease in the ratio between the area of the peaks related to C-H bending in the polymer ($2918\text{ e }2850\text{ cm}^{-1}$) and the bendings with absorption band lower than 1800 cm^{-1} . There has also been the appearance of a characteristic band for aromatic compounds in 3060 cm^{-1} .

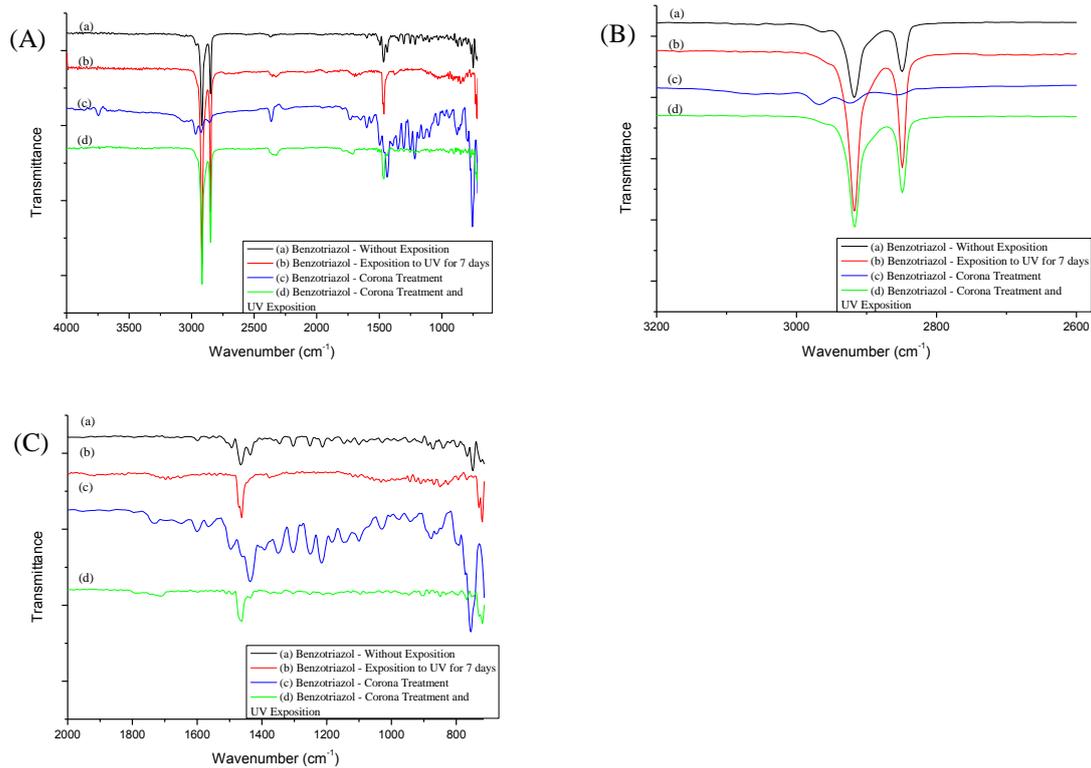


Figure 9: FT-IR spectrum for the sample with 99% of LDPE and 1% of benzotriazol. Comparison between the samples without exposition, submitted to UV radiation for 7 days, submitted to corona treatment and submitted to corona treatment with posterior exposition to UV radiation. (A) Complete FT-IR spectrum; (B) Approximation of the FT-IR spectrum between 3200 cm^{-1} and 2600 cm^{-1} ; (C) Approximation of the FT-IR spectrum between 2000 cm^{-1} and 750 cm^{-1} .

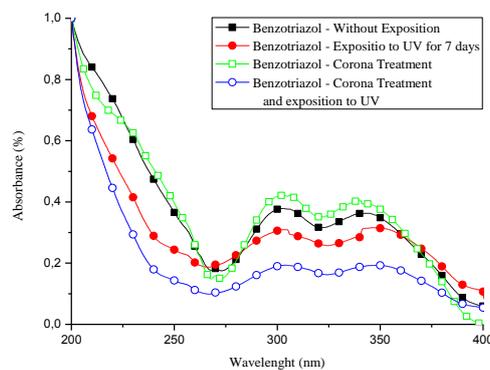


Figure 10: UV-vis spectrum for the sample with 99% of LDPE and 1% of benzotriazol. Comparison between the samples without exposition, submitted to UV radiation for 7 days, submitted to corona treatment and submitted to corona treatment with posterior exposition to UV radiation.

The UV-vis spectra suggests an increase in the absorbance region between 300 and 340 nm after corona treatment. This increase may be caused by the formation of chromophoric groups which absorb in the same region that the pre-existing groups, adding the results. Although, with the exposition to ultraviolet radiation, there was a decrease in the magnitude of these bands, which may be caused by the degradation of the molecule, agreeing with the results obtained by the FT-IR spectra, where it is shown a significant decrease in peaks related to the same.

Figures 11 and 12 shows the spectra of FT-IR and UV-vis for the sample containing 99% of LDPE and 1% of triazine. The sample submitted only to corona treatment did not show significant changes in its structure; while the samples submitted to UV radiation showed a decrease in the intensity of the peaks below 1600 cm^{-1} . The sample treated with corona treatment and posterior exposition to UV radiation presented a new peak in 1716 cm^{-1} , related to the formation of C=O bending, which indicates that after both treatments the photodegradation of the samples is started.

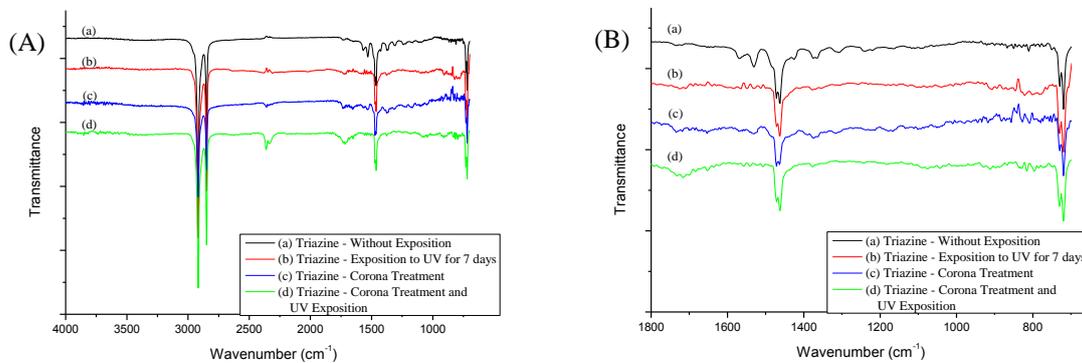


Figure 11: FT-IR spectrum for the sample with 99% of LDPE and 1% of triazine. Comparison between the samples without exposition, submitted to UV radiation for 7 days, submitted to corona treatment and submitted to corona treatment with posterior exposition to UV radiation. (A) Complete FT-IR spectrum; (B) Approximation of the FT-IR spectrum between 1800 cm^{-1} and 650 cm^{-1} ;

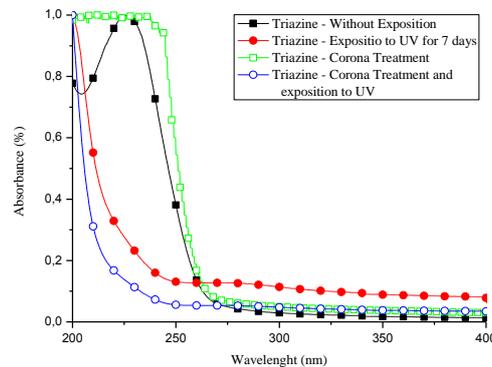


Figure 12: UV-vis spectrum for the sample with 99% of LDPE and 1% of triazine. Comparison between the samples without exposition, submitted to UV radiation for 7 days, submitted to corona treatment and submitted to corona treatment with posterior exposition to UV radiation.

By the analysis of UV-vis, it is noticed the sample that passes through corona treatment maintains the absorbance peak in 230 nm, although with higher intensity. This shows the formation of groups which absorb radiation in the same range of the pre-existing groups, adding the effects. In the samples treated with ultraviolet radiation occurred the decrease of the absorbance peak, indicating the consumption of the additive.

The results presented indicate that the better additive for LDPE to be used when the film is going to be submitted to superficial corona treatment and posterior external exposition to ultraviolet radiation, is the benzotriazol. Although this additive present lower molar absorptivity, when compared to triazine, it also shows higher resistance to the conditions in which it was exposed, maintaining its stabilizing properties after the superficial treatment.

It is noteworthy that in the analyzes done with pure additive, without its incorporation into the poly-

mer, no degradation process was observed in any of the molecules. By this time, it is possible to conclude the analyzed molecules are fulfilling their role of protecting the polymer from degradation processes.

Importantly, the results obtained from exposure to ultraviolet radiation of the additives are not consistent with actual conditions of exposure. They exhibit accelerated degradation results. By the large number of existing variables in the degradation processes, it is not possible to estimate on how much real exposure time the used the condition refers. Thus, the results obtained are merely comparative and qualitative.

4. CONCLUSION

With the analysis of the results it can be concluded the triazine is a compound which has the highest molar absorptivity. Benzophenone and benzotriazole, despite having lower molar absorptivity are compounds which absorb ultraviolet radiation in a greater spectrum range, thus ensuring greater protection of the polymer.

With the exposure of all pure compounds to ultraviolet radiation, it was noticed that in none of them, there was a structural deterioration caused by the formation of new functional groups. However, with the exposure of additivated polymeric to ultraviolet radiation, there was a decrease in ultraviolet absorption characteristic for all the compounds evaluated. However, among all the compounds, benzophenone was the only one, although it decreased the intensity of UV absorption, did not fail to protect the polymer from degradation.

With the corona treatment, there was the formation of functional groups on the surface of all films with additives. However, these structural modifications did not produce negative effect on UV absorbing property of the compounds.

With the analysis of all the results presented, it is concluded the benzotriazole is the additive best supported imposed treatment conditions, and it maintained its ultraviolet radiation absorption properties even after exposure to corona treatment and subsequent exposure to UV radiation for a period of 7 days.

The other additives analyzed undergo degradation processes and / or have been consumed during the treatments, and then are considered unfit for use as UV absorbers in LDPE during the analyzed period and for the treatment conditions tested.

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ORCID

Glaucea Warmeling Duarte	https://orcid.org/0000-0003-3847-1185
Alexandre Dal Bó	https://orcid.org/0000-0002-2289-395X
Luciano da Silva	https://orcid.org/0000-0002-1591-963X
Márcio Antônio Fiori	https://orcid.org/0000-0002-4292-2068
Camila Machado de Oliveira	http://orcid.org/0000-0002-3740-6157