

Research Article

A Comparative Study of the Photodegradation of Two Series of Cyclic Olefin Copolymers

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A series of commercial cyclic olefin copolymers (COC), namely, ethylene-norbornene (E-NB) and ethylene-tetracyclododecene (E-TD), were processed as thin films with thicknesses of 25 μm by an extrusion process. The photodegradation of neat and formulated films with different metal stearates (Fe, Co, and Mn) was investigated using an ultraviolet (UV) light lamp (340 nm) for a period of 30 days in an accelerated weathering tester model QUV from Q-LAB according to the ASTM D 5208-01 standard practice. Changes in carbonyl index (CI) and tensile properties were used to evaluate the photodegradation of the films and other properties, such as T_g variation by DSC, were also analyzed. The present study reveals that (E-NB) copolymers show higher sensitivity to photodegradation than (E-TD) resins, in the absence and presence of metal stearates. We also find that the Fe salt shows the highest oxidative activity.

1. Introduction

Polyolefins are the most produced and consumed synthetic polymers worldwide, with many uses such as packaging, toys, appliances, and disposable items. As a result of their high stability and resistance to degradation, these compounds have accumulated in the environment, contributing to many ecological and pollution problems. Natural weathering (including solar radiation), wind, and ambient temperatures lead to the formation of free radicals in these compounds, when combined with oxygen. The oxidative degradation process may take many years to reach complete degradation. The technologies most commonly used to accelerate the degradation process [1] involve the use of prooxidant additives (POA) to make polyolefins oxobiodegradable [2].

Polymer photodegradation and stabilization are extensive fields of study. It is well established that photooxidation reactions play an important role in the degradation process of ultraviolet (UV) irradiated polymeric materials, and the controlling mechanisms have been studied by some authors [3–5]. The physicochemical changes which occur during photooxidative reactions are characterized by an increase in the concentration of the oxygen-containing groups such

as peroxides, hydroperoxides, and ketonic carbonyl groups [6]. However, cross-linking and chain scission processes, detected during a study of photooxidation in polyethylene, are believed to be sources of great importance in causing changes in the mechanical properties of polyolefins [7].

Nowadays, several authors have already studied the influence of (POA) on the photooxidation of polymers; for instance, Pablos and coworkers [8] studied the effect of iron and calcium stearates on the photodegradation of polyethylene (LDPE and LLDPE) under natural and artificial exposure using chemiluminescence. Changes in chemical structure were monitored through Fourier transform infrared spectroscopy (FTIR) and gas chromatography-mass spectrometry (GC-MS) was used to follow changes in molecular weight and the content of degradation products. Ojeda et al. [9] prepared different films from high density polyethylene (HDPE), linear low density polyethylene (LLDPE), and isotactic polypropylene (PP) containing antioxidant additives and exposed them to natural weathering for one year, during which their structure, thermal, and mechanical properties were monitored. Roy and coworkers [10, 11] used cobalt and manganese stearates to study the photo and thermooxidative degradations of LDPE and LLDPE. The study showed that

TABLE 1: Description and properties of cycloolefin copolymers used in this study (data provided by the suppliers).

Supplier	Code	T_g °C	% of NB units	% of TD units	Density g-cm ⁻³	MFI g/10 min ^a	Series ^b
Topas®	6013	140	54.3		1.02	1.00	D
Topas	8007	80	37.6		1.02	1.70	D
Apel	6509	80		21.6	1.02	1.51	A
Apel	8008	70		19.5	1.02	1.02	A

^aAt 190°C and 2.16 Kg; ^b[12].

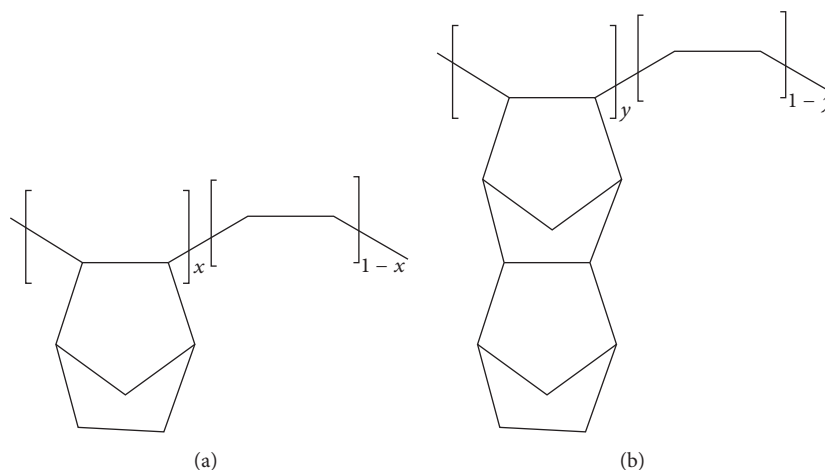


FIGURE 1: Structure of COC copolymers. (a) Ethylene-norbornene (E-NB) copolymer: Series D. (b) Ethylene-tetracyclododecene (E-TD) copolymer: Series A.

the durability of the olefin polymers was less than one year, as a consequence of severe oxidative degradation. The main factors influencing the degradability were the frequency of tertiary carbon atoms in the chain and the presence of POA.

Zalikhha and coworkers [12] studied the effect of cobalt stearate on photooxidative aging of polypropylene film, reporting the changes in tensile properties and carbonyl index. In their work, they concluded that the rate of degradation was enhanced and dependent on the concentration of cobalt stearates.

Cycloolefin copolymers (COCs) form a new class of copolymers which possess excellent properties, such as totally amorphous structure, a high glass transition temperature, excellent mechanical and optical properties, high decomposition temperature, and good moisture barrier, making them a potential replacement in some engineering polymers. These novel copolymers have diverse applications in optical fibers, electrical appliances, automotive parts, containers, bottles, compact disks, and packaging films.

As a film, COC resins offer significant advantages over existing products, especially when high water vapor barrier, clarity, and rigidity are required [13]. Their applications cover a broad spectrum ranging from high moisture barrier packaging films to technical films capacitors [14, 15]. Shrink films for sleeves and flexible films based on blends of COCs with low density polyethylene have also been developed [16].

Recently, there have been many articles devoted to the investigation of the structure and mechanical properties of

these new COCs using standard investigative methods; however, scarce research on their photo- and thermal degradation has been completed, compared with similar products made from olefin polymers. The aim of this investigation is to make a comparative study of stability under the influence of UV irradiation of two neat and metal formulated series of COCs.

2. Experimental

2.1. Materials. COCs (6013 and 8007) supplied by Ticona (Kelsterbach, Germany) and COCs (6509 and 8008) from Apel (Mitsui Chemicals, Inc.) were used for the preparation of the thin films. Some physical properties of these two copolymers are listed in Table 1 and are represented by structures (a) and (b), respectively, in Figure 1 [17]. Prooxidant additives, as a master batch of three different transition metal (Fe, Co, and Mn) stearates, were provided by different suppliers (d2w: from Symphony Environmental Ltd.; Reverte BD93470: from Wells Plastics Ltd.; and EPI: from Environmental Products Inc.) and used as recommended for the production of commercial products (Table 2).

2.2. Sample Preparation. In this study, each COC was dry mixed with 1.0 wt% of each metal stearate and fed into a Killion single screw extruder KTS-100 (one-inch diameter and $L/D = 24:1$) at a constant screw speed of 100 rpm and a collection rate of 5.4 m/min. For the Topas resin 6013, the temperature settings for the extruder were feed zone, 220°C; compression zone, 250°C; metering zone, 260°C; and die

TABLE 2: Active metals and content of prodegradant agents in master batch.

Prodegradant agent	Active metal	Metal content (ppm)
d2w	Manganese	3399
Reverte	Iron	659
EPI	Cobalt	9058

zone, 270°C. For the rest of the copolymers, the temperature settings were feed zone, 190°C; compression zone, 210°C; metering zone, 210°C; and die zone 230°C. A 30.5 cm wide flexible lip die was adapted to produce the cast film; samples with a size of $1 \times 14 \text{ cm}^2$ were cut for the aging process.

2.3. UV Aging Tests. The cycloolefin film samples were exposed to aging in a QUV accelerated weathering tester according to ASTM D 5208-01 for 30 days (720 hr) for photooxidative treatment. Single samples were withdrawn every five days and changes due to photooxidation were monitored by recording changes in mechanical properties and the molecular structure.

2.4. FTIR Analysis. Molecular changes upon UV light exposure were investigated using FTIR Avatar 330 Thermo Nicolet equipment. The test on the film was conducted using an IR band between 4000 cm^{-1} and 450 cm^{-1} ; spectra were made up of 25 scans with the resolution set to 4 cm^{-1} . Carbonyl index (CI) was used to monitor the level of degradation of the cycloolefins. It is defined as the ratio of absorbance of the carbonyl band at $1680\text{--}1840 \text{ cm}^{-1}$ (which is a by-product of the photooxidation) and internal thickness absorption band at 1456 cm^{-1} . These have been calculated by the baseline method [18, 19].

Carbonyl Index (CI)

$$= \frac{\text{Absorption at the maximum of carbonyl band}}{\text{Absorption at } 1456 \text{ cm}^{-1} \text{ (internal thickness band)}} \quad (1)$$

2.5. Tensile Tests. Tensile tests for all samples were evaluated according to ASTM D882 method at room temperature. Tests were performed on films with a constant thickness of $25 \mu\text{m}$ and same dimensions $1 \times 14 \text{ cm}^2$ using an Instron 4301 tensile tester with a load cell of 500 N with a 0.1 N sensitivity and an electrical sensitivity of 1.6 mV/V with a constant cross head speed of 0.50 cm/min. An average value from five tested samples was taken for each film.

2.6. DSC Analysis. DSC tests were conducted using a Q200 TA Instruments calorimeter, under a nitrogen flow of 100 ml/min^{-1} . The samples were first heated from 20 to 350°C at $10^\circ\text{C/min}^{-1}$ and held at 350°C for 1 min to delete thermal history. After that, the samples were cooled down to 20°C with a cooling rate of 20°C/min and held at 20°C for 1 min. The second run was performed by heating the sample to 350°C under the same conditions as the first run; these scanning steps can be seen for Topas 6013 resin in Figure 2. On the first run we can appreciate some stresses built into

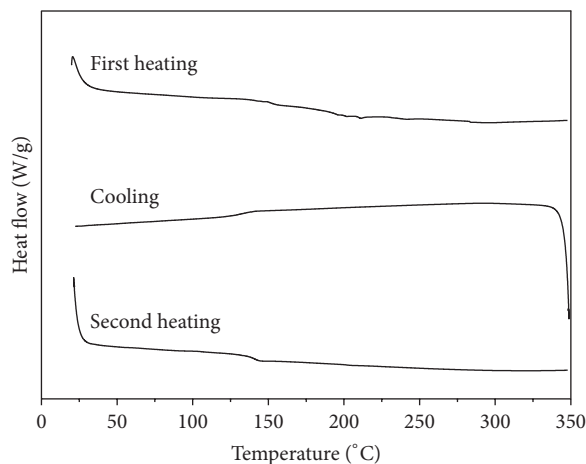


FIGURE 2: DSC traces of the Topas 6013 resin.

the material as a result of processing, handling, or thermal history around 140°C (related to the glass transition) and on the region of $200\text{--}275^\circ\text{C}$ which are released when the material is heated through its glass transition.

The data used in this publication were taken from the second heating to evaluate the glass transition temperature (T_g) of each copolymer with and without metal stearates after aging. On a previous work [20] we published the high thermal stability of these cycloolefin resins with a decomposition temperature above of 450°C . The very low CI values and the little difference on the mechanical properties reflected on the percent in elongation at break indicate a good stability to oxidation even under the presence of prodegradant additives at the thermal aging conditions. Similar results on thermal stability of cycloolefins have been reported by Yang and coworkers [21] and an investigation on the role of metal stearates on the degradation behavior of LDPE has been published by Roy and coworkers [22].

3. Results and Discussion

Physicochemical changes which occur during photooxidative reactions are characterized by an increase in the concentration of the oxygen-containing groups such as peroxides, hydroperoxides, and also the ketonic carbonyl groups [23, 24]. However, cross-linking and chain scission processes occurring during photooxidation in polyolefins are believed to be sources of great importance in causing changes in the mechanical properties of these materials [25]. Normally, it has been reported [26] that initial values of mechanical properties are not affected by the incorporation of POA additives, thereby implying that these additives do not lead to degradation until being activated by UV light or high temperatures.

3.1. FTIR Studies. The relative effects of the transition metal additives on the photodegradation of the series of cycloolefins were compared by simultaneous irradiation on the neat and formulated films using UV light in a QUV accelerated weathering tester. As shown in Figure 3, the infrared spectrum

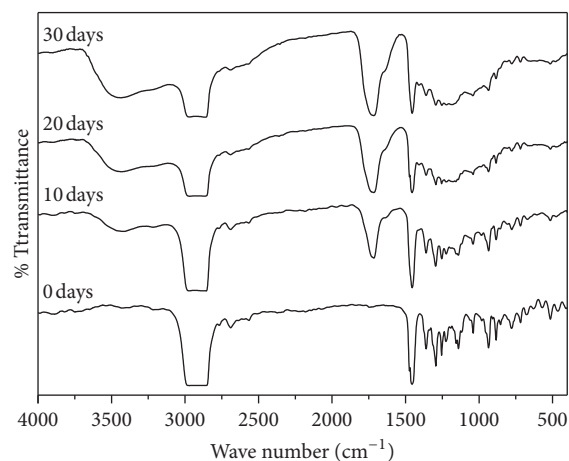


FIGURE 3: Change in IR of COC 6013 neat film during photoirradiation.

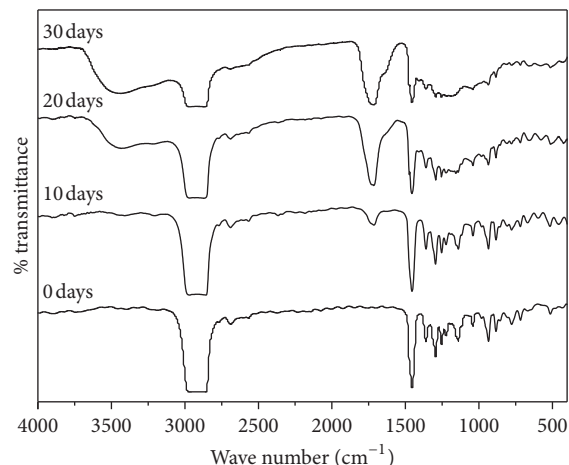


FIGURE 4: Change in IR of COC 6013 containing Fe prodegradant during photoirradiation.

of a COC 6013 neat film changes remarkably in the regions of ca. 1720 cm^{-1} due to carbonyl groups, $3300\text{--}3400\text{ cm}^{-1}$ due to hydroxyl groups, ca. 1300 cm^{-1} due to an amorphous region, and ca. 909 cm^{-1} due to unsaturated groups after 30 days of UV irradiation. The presence of the vinyl signal (909 cm^{-1}) could be explained that during the extrusion process in presence of air and high temperature an eventual degradation of the resin by thermooxidation gives rise to this signal [27, 28]. The absorption band around 1714 cm^{-1} , which can be assigned to the stretching of $>\text{C}=\text{O}$ functionalities, increases in intensity and broadened substantially, indicating the presence of multiple oxidation products [29, 30].

In addition, infrared spectra of COC films containing prodegradant additives are shown in Figure 4, where the extent of the changes in these regions of the infrared spectra is apparently affected by metal additives present on the sample films.

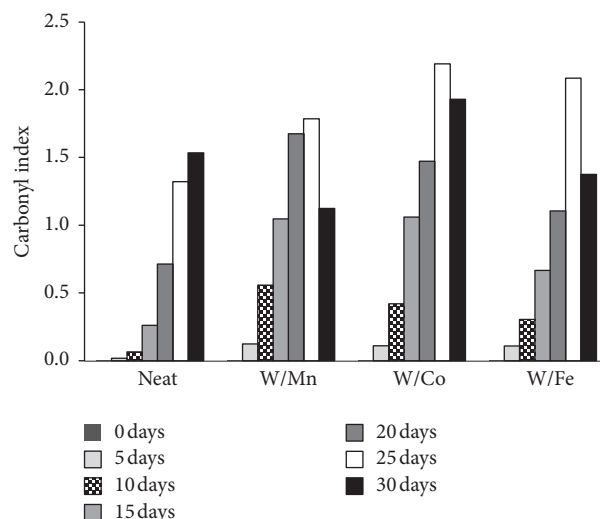


FIGURE 5: Increase in the carbonyl index of Topas 6013 COC neat and formulated films during exposure to QUV irradiation.

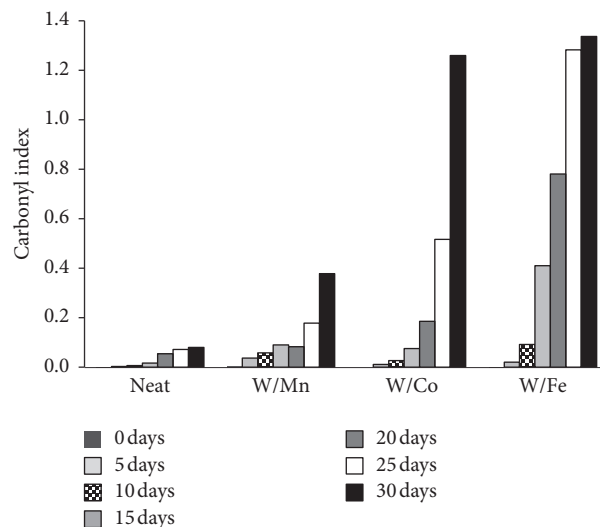


FIGURE 6: Increase in the carbonyl index of Topas 8007 COC neat and formulated films during exposure to QUV irradiation.

The extent of degradation of these samples under the influence of metal additives has been quantified by calculating the CI, which is the ratio of the intensity of signals ($1740/1456\text{ cm}^{-1}$) at different times of exposition. This increase in CI with time of exposure indicates an advance of the degradation reaction, as a result of the decomposition reactions of peroxides and hydroperoxides generated by the formation of free radicals responsible for the beginning of the degradation process, which has been observed on other polyolefins [22, 31]. Figures 5–8 represent the change in the CI as a function of exposure time of UV light on the neat and formulated films.

We can see in Figure 5 that the Topas COC 6013 film is relatively more susceptible to degradation even without metal stearates and this can be explained by the presence

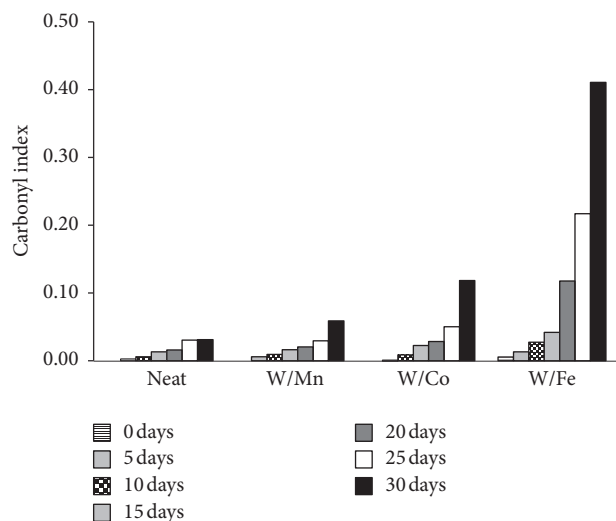


FIGURE 7: Increase in the carbonyl index of Apel 6509 COC neat and formulated films during exposure to QUV irradiation.

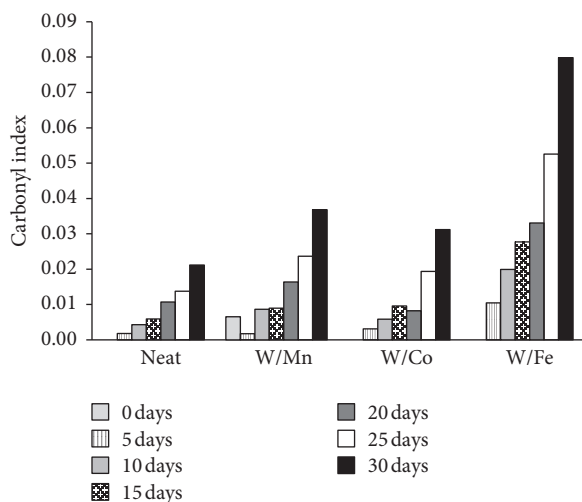


FIGURE 8: Increase in the carbonyl index of Apel 8008 COC neat and formulated films during exposure to QUV irradiation.

of a large number of norbornene units on the backbone copolymer, which increases the number of tertiary weak sites for oxidation [32]. Also it is observed that at 30 days of exposure the carbonyl index decreases when it is formulated with the three stearates; this reduction can be explained to the fact that the degradation is occurring through a stage in which the cross-linking predominates more than molecular excision, since these two phenomena are happening simultaneously as it was reported by Kyrikou et al. [33] and by Nikolic and coworkers [34], when cross-linking predominates, species with carbonyl groups are reduced. Also, Wypych [35] reports that the concentration of C=O decreases during exposure to UV light because this functional group is susceptible to undergoing photooxidation reactions by UV radiation effects, so the carbonyl index decreases. Another explanation for this behavior could be that the

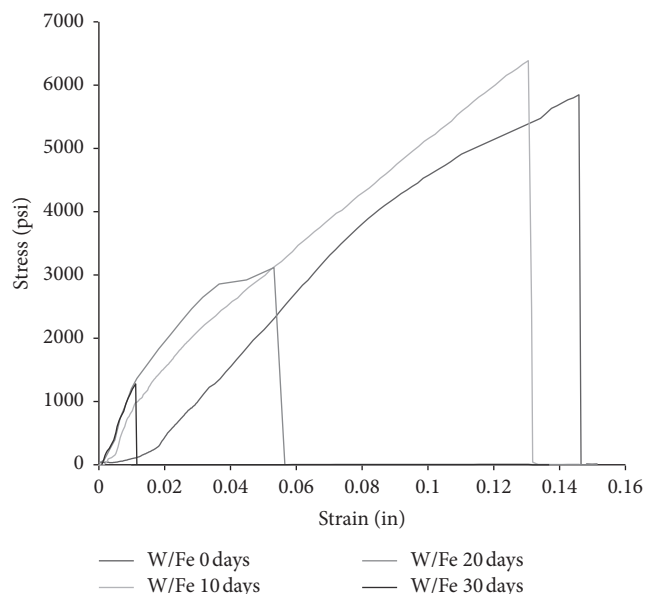


FIGURE 9: Stress-strain curve for the Apel 6509 resin with Fe additive.

photolysis of carbonyl products (such as carboxylic acids, aldehydes, and/or lactones) to volatile products leads to a lower concentration of oxidation products in the polymer during photodegradation [36].

With respect to the two evaluated series, the Apel 8008 COC copolymer showed higher photooxidative stability, even in the presence of prooxidants, as can be seen by the lower values of the CI during the aging time, and this stability is associated with the low norbornene content, which implies lower C-H labile bonds.

By comparing the prooxidant nature of the three stearates on both series of COCs, we can conclude that the Fe and Co stearates are more active than the Mn stearate.

3.2. Mechanical Properties. Elongation at break of the films was evaluated at regular time intervals to monitor the degradation behavior, as it has been considered to be a direct indicator of this property [37, 38]. Figure 9 presents a stress-strain curve for the Apel 6509 resin with Fe additive showing the loss of the mechanical properties during 30 days of UV aging. Figures 10–17 present the effect of photooxidation on elongation at break and tensile stress at break of neat and formulated films. The elongation at break values decreased for the neat samples and for those containing metal stearate salts, the rate is much faster in the case of Fe and Co metals.

Photooxidation is a process where competition between bond breaking and cross-linking happens during aging and this can explain the low and high values of elongation of the samples. The Topas 6013 COC films containing metal stearates became completely fragile after 15 days of photooxidation treatment and could not be tested further. However, it is noted here that the elongation values of neat Topas COC films dropped faster than those of the Apel copolymers, which means that the former are less stable to photooxidation due to the presence of high content of norbornene rings and

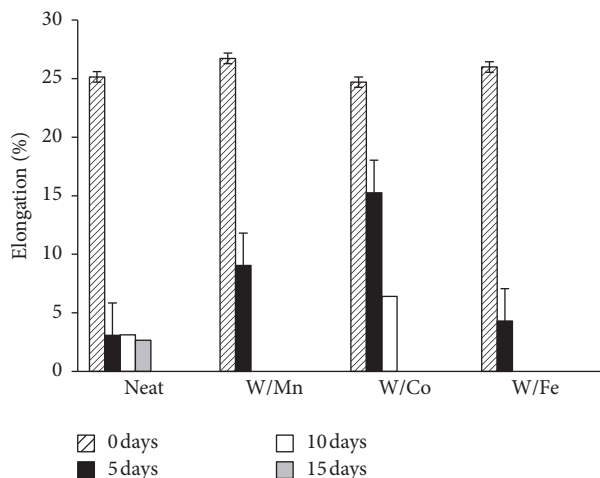


FIGURE 10: Elongation at break of Topas 6013 COC neat and formulated film with different POA.

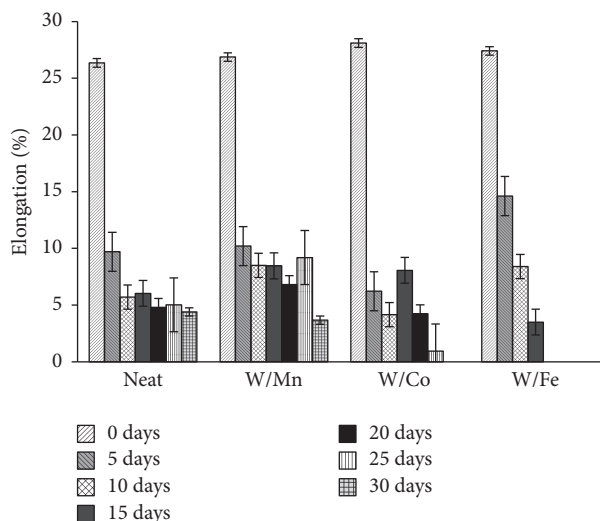


FIGURE 11: Tensile stress at break of Topas 6013 COC neat and formulated films with different POA.

therefore higher content of tertiary carbons susceptible to degradation.

Regarding tensile stress properties, an erratic trend in the strength values with the progress of the degradation process for the different formulations is observed in Figures 11, 13, 15, and 17; this behavior may be related to the mechanism of the degradation reaction and the stages through which this process occurs. The increase in tensile strength as the photodegradation takes place may be related to a reaction step in which cross-linking reactions predominate and the latter decrease is a result of chain scission [23, 39].

Tanaka and coworkers [40] published the effect of the morphology on the photodegradation of LDPE films with UV light and reported that chain scission lowers the molecular weight, whereas cross-linking reaction causes an increase in the higher molecular weight fraction and these changes

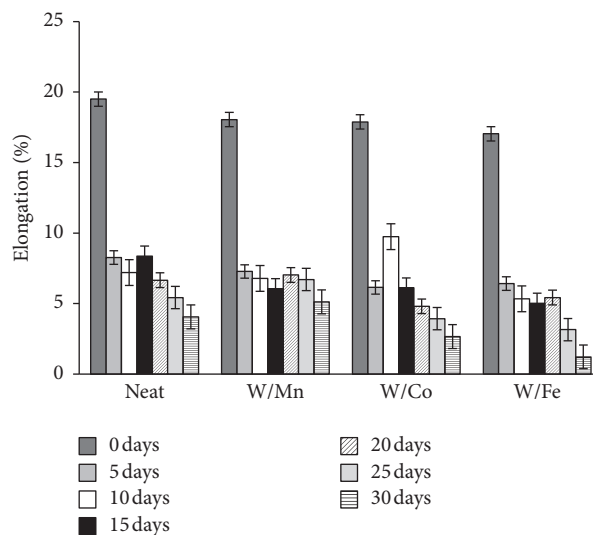


FIGURE 12: Elongation at break of Topas 8007 COC of neat and formulated films with different POA.

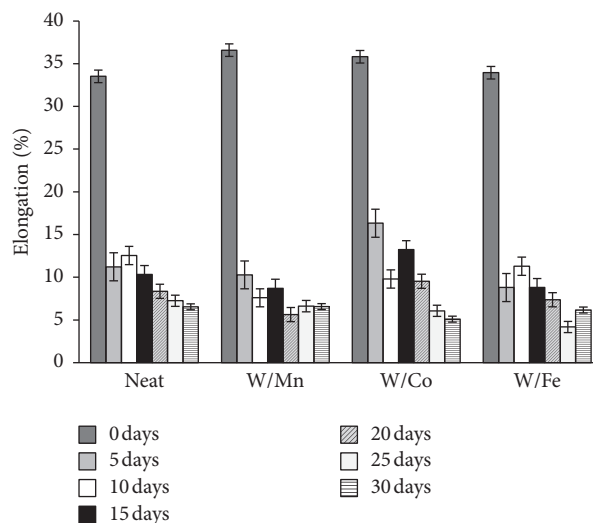


FIGURE 13: Tensile stress at break of Topas 8007 COC neat and formulated films with different POA.

which occurs simultaneously during photodegradation could explain the behavior reported on elongation and stress at break during aging.

The photooxidative behavior was found to depend upon the type of metal present in the COC matrix and follows the order of $Fe > Co > Mn$.

3.3. Thermal Properties. DSC thermogram for the Topas 8007 resin is presented in Figure 18; this figure shows the first heating run, cooling, and second heating run. The first run shows a change of slope at $80.5^{\circ}C$ with an apparent melting at glass transition (T_g) due to the stresses built into the material as a result of processing, handling, or thermal history which are released when the material is heated through its glass transition.

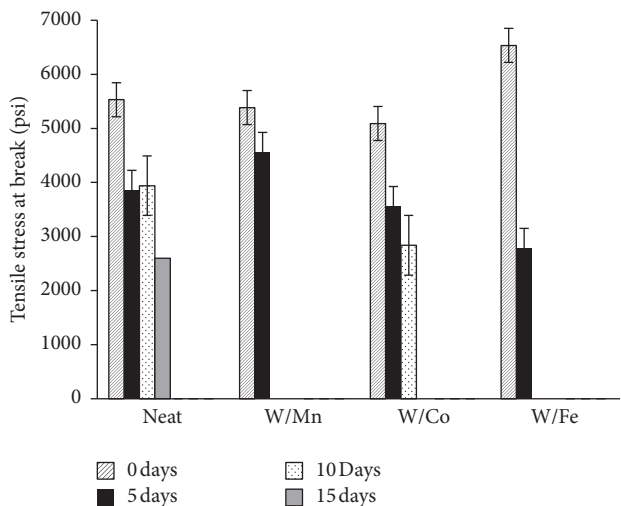


FIGURE 14: Elongation at break of Apel 6509 COC neat and formulated films with different POA.

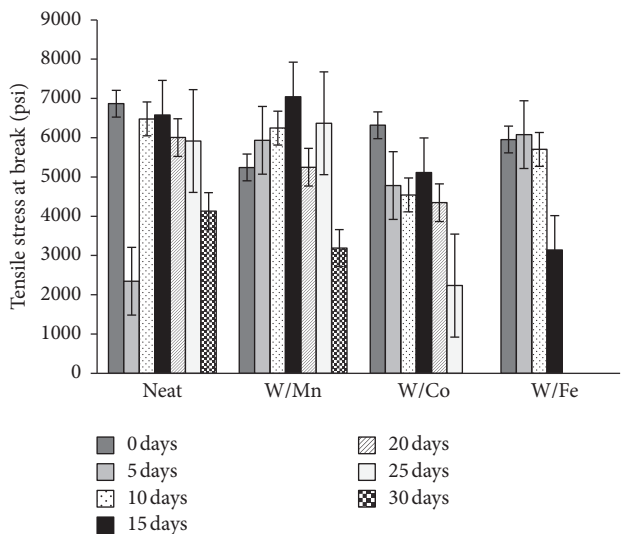


FIGURE 15: Tensile stress at break of Apel 6509 COC neat and formulated films with different POA.

During the quench cooling from 350°C to a temperature below T_g , the thermogram does not show an exothermic signal associated with a crystallization phenomenon because the polymer is amorphous; however, a little change on the slope of the curve can be seen at 77.5°C due to the transition of the rubbery to glassy state of the polymer associated with the T_g temperature.

The second heating run after the internal stresses were relieved; the graph shows a change on the flow energy manifested by the presence of the glass transition at 79.7°C when the molecules go from a rigid to a flexible structure.

Figures 19 and 20 present the heating DSC traces of the neat and formulated COC samples after 30 days of aging; as shown, there exists a drop in the (T_g) between the UV treated and untreated samples, which implies a chain scission of the copolymers which is accelerated by the influence of the

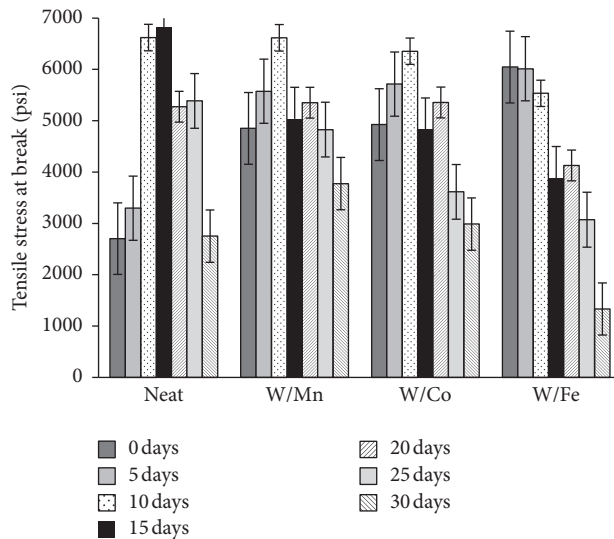


FIGURE 16: Elongation at break of Apel 8008 COC neat and formulated films with different POA.

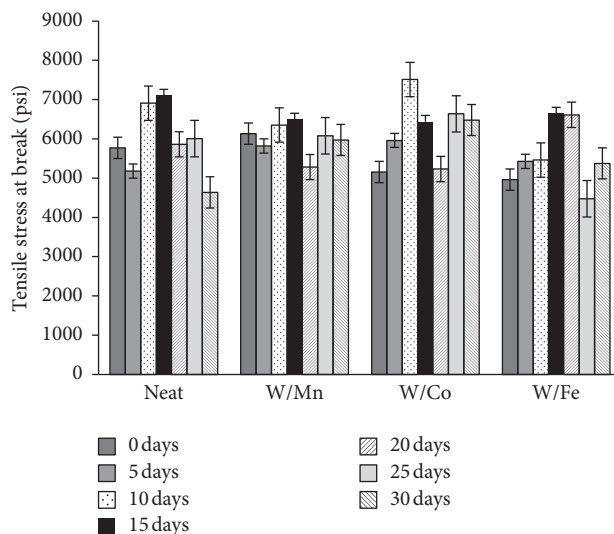


FIGURE 17: Tensile stress at break of Apel 8008 COC neat and formulated films with different POA.

prooxidant additives, as shown in Table 3. Here, we can see that the Fe stearate shows the highest reactivity based on the higher difference on the drop of the T_g value, followed by Co and finally the Mn salt.

Table 3 also shows the T_g values obtained from the difference with the T_g of neat film, and as it is seen, the Apel 8008 COC resin shows the lowest change on T_g values in comparison with the other resins; this behavior could be associated with the great stability of its structure, which was observed by the lowest CI values in the Figure 8; its resistance to oxidation is due to the low content of norbornene rings and therefore lower content of tertiary carbons susceptible to degradation. However, even when the resin is stable to chemical oxidation, the generation of free radicals during treatment with UV light promotes cross-linking reducing the

TABLE 3: T_g value of COC films formulated with different prooxidant additives after 30 days aging under UV light.

	6013		8007		6509		8008	
	T_g (°C)	Δ °C	T_g (°C)	Δ °C	T_g (°C)	Δ °C	T_g (°C)	Δ °C
Neat film	139.6		79.7		79.4		67.4	
UV treated film	132.5	7.1	80.0	0.3	78.7	0.7	66.9	0.5
w/Mn	129.8	9.8	77.3	2.4	77.8	1.6	64.1	3.3
w/Co	128.5	11.1	74.3	5.4	76.2	3.2	64.6	2.8
w/Fe	128.3	11.3	72.1	7.6	75.8	3.6	64.6	2.7

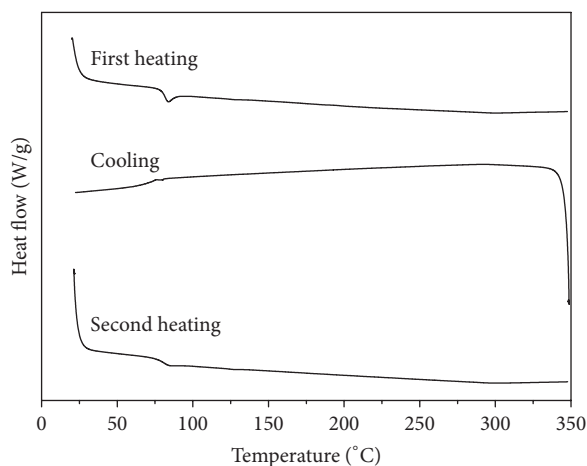


FIGURE 18: DSC traces of the Topas 8007 resin.

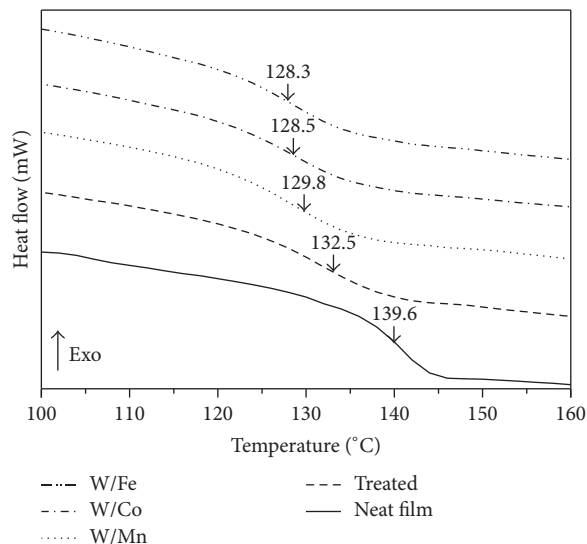


FIGURE 19: DSC traces of the Topas COC 6013 neat and formulated films with POA after 30 days of aging under photoirradiation.

molecular mobility by the chemical bonds formed between polymer chains, causing a decrease of the elongation against an effort [41] and stiffening of the film, making it a brittle film but retaining its thermal properties, with a little noticeable change in T_g .

The degradation process of a polymeric material can occur through several mechanisms that bring about chemical

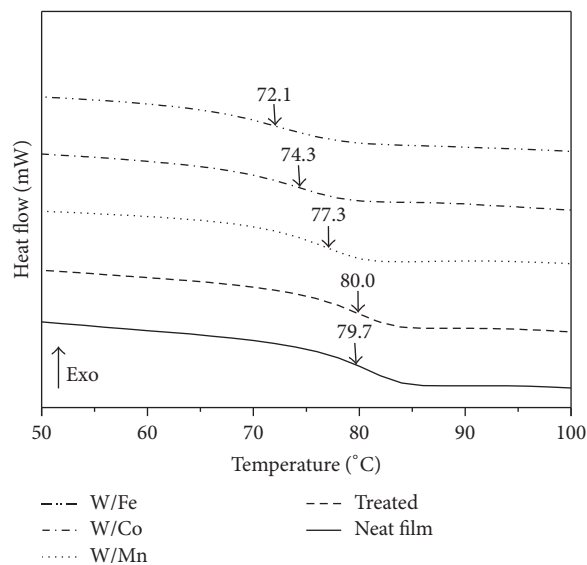


FIGURE 20: DSC traces of the Topas COC 8007 neat and formulated films with POA after 30 days of aging under photoirradiation.

and structural changes of the material affecting the mechanical properties of the material [42, 43]. Molecular scission, which has the direct effect of lowering the molecular weight, will reduce the elasticity of the material, while possible cross-linking reactions may cause stiffening of the polymer. These changes will be reflected in the mechanical properties, specifically in elongation and tensile strength. As it was shown in the figures of mechanical properties, even when the virgin resins showed loss of properties with aging, the presence of the POA additives accelerated the degradation process due to the generation of free radicals which catalyze the reaction.

Regarding the formation of carbonyls in the different resins, their presence was increased with the time of UV treatment; however, there exists no correlation between mechanical properties and Carbonyl index because tensile properties of films do not change at the same rate as carbonyl groups formation [44].

Kinetic study and mechanism of oxidation for this system are in progress and the results will be published later.

4. Conclusions

The present study reveals the different behavior of photostability for two cycloolefin series, in the presence and absence

of oxidative salts, under UV irradiation. COC 6013 was found to be more susceptible to degradation than the rest of the copolymers due to the presence of a high percent of norbornene units in its structure, which increases the number of tertiary sites that are sensitive to UV irradiation and leads to the generation of free radicals, promoting the degradation of the copolymers.

Also, this work shows that Fe stearate had the highest effect on the cyclic olefin oxidation, followed by the Co and Mn salts, as observed by the carbonyl index, elongation, and T_g measurements. This behavior can be explained by the catalytic effect generated by the ability of the metals to switch between two consecutive oxidation states leading to the formation of free radicals, which in turn generate the decomposition of hydroperoxides.

The lability of two COC series, in the presence of transition metal stearates, during the aging process, shows the following degradation order: COC 6013 > COC 8007 > COC 6509 > COC 8008. Copolymers with tetra cyclododecene comonomer units (Series A, Apel) are more stable to photodegradation than those which have norbornene as the comonomer units (Series D, Topas), and this difference is associated with the percentage of tertiary carbons in their molecular structure.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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