

## Accelerated aging of ethylene – norbornene copolymers containing transition metals stearates

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Cycloolefin copolymers are used in different engineering applications and have been considered as packaging materials due to their brightness and transparency. For this application, it is relevant to study their degradative behaviour. The use of pro-degradant additives containing metal ions, which accelerate oxo - degradation, has been proposed to improve degradability of conventional polymers in the environment. In this research, ethylene-norbornene copolymers mixed with iron and manganese stearates were used as raw material to manufacture extruded flat films with thickness of  $50 \mu\text{m} \pm 5 \mu\text{m}$ . The films were subjected to accelerated conditions of photo-oxidative and thermo-oxidative degradation. Degradation was monitored through the measurement of tensile mechanical properties, infrared spectroscopy and carbonyl index. As a result, it was evidenced that pro-oxidants accelerated property changes in the films subjected to different degradative conditions. The carbonyl index showed the progress of the degradation reaction. Iron stearate had greater influence on films properties under photo-oxidative conditions, while the films containing manganese stearate demonstrated greater influence under thermo-oxidative conditions.

### 1. Introduction

The ethylene norbornene copolymers are a type of cycloolefins characterized by its rigid chemical structure due to cyclic units in the polymer main chain (Arndt-rosenau & Beulich, 1999). In consequence, this polymer is amorphous, and exhibit high glass transition temperatures, high thermal stability, transparency, low shrinkage and low humidity absorption (Liu et al., 2007). All mentioned properties made this materials competitive to high-performance thermoplastic polymers as polycarbonate and poly (methyl methacrylate) (Cichosz et al., 2019). Transparency and impermeability are appropriate for diverse packaging applications such as blisters for drugs in solid form (Lago et al., 2017), in which degradability is an important topic to study. Figure 1 shows the repetitive unit of the ethylene norbornene copolymer.

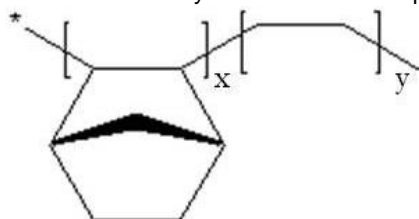
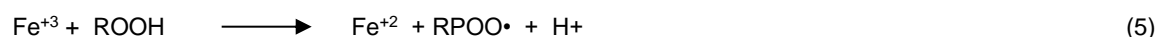
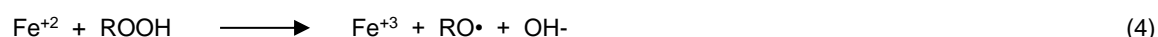


Figure 1: Chemical Structure of ethylene norbornene copolymer (Liu et al., 2007).

## 1.1 Polymer Degradability

It is known that polymeric materials without heteroatoms such as oxygen and functional groups such as carbonyl are not biodegradable, due to their long times of decomposition in environmental media (Selke et al., 2015). Since ethylene norbornene copolymers are not biodegradable, their use is negative for the environment (Schmid et al., 2020). Different possibilities have been researched to improve the situation. Some proposals introduce heteroatoms to the main chain of non-biodegradable polymers, while other use pro-oxidant additives in polymer formulation (Singh & Sharma, 2008). Some innovative alternatives as add cellulose to ethylene – norbornene copolymers, have been tested to improve the degradative behaviour of these materials (Cichosz et al., 2019). Different research groups around the world have studied the effect of oxidant agents such as metal stearates or another chemical substance that allow metal ions act as a catalyst of the oxidation reaction. Metal carboxylates promote the radical formation from the decomposition of peroxides and hydro peroxides that are by products of the polymers thermal and photo-oxidation. Reactions 1 to 5 show the possible steps during oxo-degradation of polymers and the catalyser action of metal ions during the process. Different mechanisms have been proposed for the action of metal ions as catalysers of the oxidation reaction of the polymer. In general, it is known that the metal ions act in the breakage of the peroxide, hydro peroxide and alkoxide radicals, as observed in Equations 1 to 5, where  $R\cdot$  is a polymeric radical that reacts with oxygen to form a hydro peroxide radical. This radical reacts with another polymer molecule to obtain a polymeric radical and a hydro peroxide. Besides, the metal ions catalyse the hydro peroxide decomposition to form peroxide and alkoxide radicals (Singh & Sharma, 2008).



Previously, experimental studies have been developed about metal ions as promoting agents of oxo-degradation in polyolefins (Roy et al., 2007). These works used the Carbonyl Index (CI) as an indicative parameter of the degradation reaction advance (Chiellini et al., 2006). Besides, previous research have shown that mechanical properties suffer an accelerated decrease in presence of metal ions (Roy et al., 2009).

To analyse the effect of metallic stearates on degradation of cycloolefin copolymers, Zavala and Gutierrez used this kind of polymers in presence of commercial pro-oxidant additives. The research reported the loss of mechanical properties, changes in the CI and the effect on thermal properties during the degradation (Gutiérrez-Villarreal & Zavala-Betancourt, 2014).

In this research ethylene norbornene copolymer was mixed with metal stearates of iron and manganese to study the effect of each metal ion upon the degradative process and the chemical reaction of thermal and foto - oxidation.

## 2. Experimental

### 2.1 Materials

Mixes of cycle olefin copolymers and pro degradant agents were prepared. The selected copolymer was Ethylene Norbornene with 30% mol of cyclic units (**C**) from TOPAS Advanced Polymers GmbH and glass transition temperature of 65 °C. As degradant additives, ferric stearate and manganese stearate from Santa Cruz Biotechnology were used.

### 2.2 Film Preparation

Masterbatch of metal stearates dispersed in **C** were prepared using an internal mixer (Plasti-Corder, C. W. Brabender Instruments Inc) at 220 °C. The products were pelletized in a Morelli single screw extruder with L/D of 12, a single hot zone of 180 °C and extrusion rate of 23 rpm. The pelletized masterbatches were extruded with pure **C** through a flat die of 12 inches wide, using a temperature profile between 180 °C and 230 °C. Films of 50  $\mu\text{m} \pm 5 \mu\text{m}$  were obtained. The resulting films had 0.3 wt% and 0.5 wt% of each metal stearate and are named with the letter C from copolymer, followed by F from ferric stearate or M from manganese stearate, and the number 1 for 0.3 wt% or 2 for 0.5 wt%.

### 2.3 Aging test

Samples of each formulation were cut into rectangles of 13 mm wide and 130 mm high. The samples were exposed to thermo-oxidative and photo-oxidative conditions. In each case, degraded samples were removed at different previously established times and subjected to tensile mechanical test and infrared spectroscopy. The samples aged under dark thermo-oxidative conditions in a forced convection oven at 70°C for 170 days, according to ASTM D 3012 standard. Moreover, photo-oxidation was carried out in an aging test chamber QUV from Q-LAB using irradiation of  $0.78 \pm 0.02 \text{ W/m}^2\text{nm}$  at 340 nm. The cycle included 20 h of UV irradiation with a temperature of  $50 \pm 3^\circ\text{C}$  and 4 h of condensation under  $40 \pm 3^\circ\text{C}$ .

The mechanical properties were measured in a Tinius Olsen Testing Machine according to ASTM D 882 standard. The spacing between the claws was 100 mm, the crosshead speed was 12.5 mm/min and a load cell of 50 N was used. About five samples were tested for each condition and the average value was reported. To determine the influence of ion type and degradation time upon mechanical properties a Tukey statistical test was performed.

The infrared spectra were obtained with an Avatar 330 Thermo Nicolet FTIR, using IR band length between  $4000 \text{ cm}^{-1}$  and  $400 \text{ cm}^{-1}$ . The spectra were taken by duplicate at an average of 25 scans with  $2 \text{ cm}^{-1}$  resolution. The absorbance IR spectra data were used to calculate the carbonyl index (CI), defined as a ratio between carbonyl absorbance signal around  $1712 \text{ cm}^{-1}$  and the absorbance signal at  $1456 \text{ cm}^{-1}$  due to  $\text{CH}_2$  rocking mode peak, as calculated by the base line method (Roy et al., 2009).

### 3. Results and Discussion

Figure 2 shows the chemical changes caused by thermal and photo-oxidative conditions on the pure and formulated cycloolefin copolymer. Figure 2 (a) evidences the appearance and growth of signals related to the resulting chemical groups during the photo-oxidation reaction, first of all, the signal around  $1,712 \text{ cm}^{-1}$ , which corresponds to carbonyl groups formed during the oxidation reaction of polymer (Ali et al., 2016). Another important change is a signal around  $3,400 \text{ cm}^{-1}$ , due to the OH groups that are formed during the degradative process (Dixit et al., 2016). Similarly, Figure 2 (b) presents the degradative behaviour of the pure cycloolefin copolymer under thermal oxidation. In this case, there is no change in the IR signals of the polymer, even though the degradation time was 170 days, while for the photo-oxidation it was just 28 days. The difference in exposition times is an evidence of the accelerated loss of properties in the pure copolymer as an effect of UV radiation.

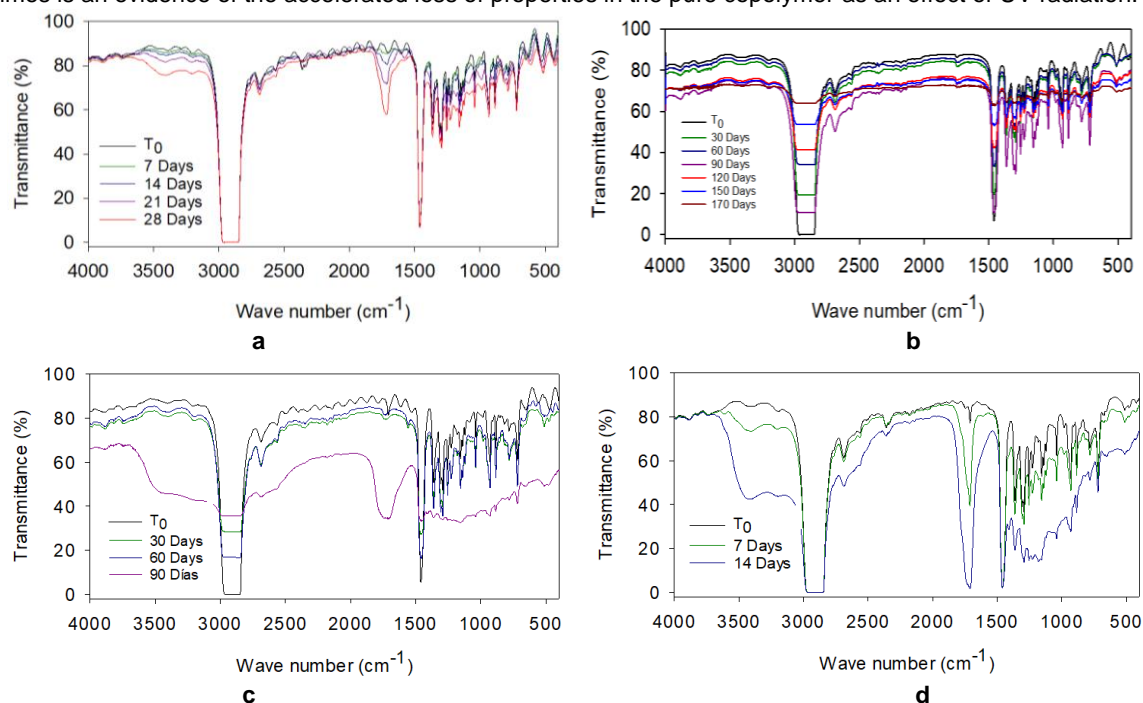


Figure 2: FTIR spectra of cycloolefin copolymer pure and blended with metal stearates. (a) Photo-oxidised pure cycloolefin copolymer, (b) thermo-oxidized pure cycloolefin copolymer, (c) thermo-oxidized CM2, and (d) photo-oxidised CF2.

Figures 2 (c) and (d) show the FTIR spectra of ethylene – norbornene copolymer blended with metal stearates as pro-degradant agents. In Figure 2 (c), the formulation CM2 presents a wide and deep peak at  $1,712\text{ cm}^{-1}$  after 90 days of exposition to temperature. Before 90 days, the carbonyl signal is small, afterwards, it was not possible to perform the test due to damage in the samples that made it impossible. Figure 2 (d) shows the FTIR spectra of CF2 blends exposed to UV radiation. In this case, the samples lost their stability after 14 days of the test. The carbonyl signal of the polymers containing metal stearates under photo degradation shows deep and sharp peaks after few days of exposition, but the CF2 shown in Figure 2 (d) was the formulation with the deepest signals of carbonyl in all the prepared samples.

The presence of carbonyl signals at  $1,712\text{ cm}^{-1}$  could be an evidence of the degradation advance. In this sense, the FTIR absorbance signal is used as a parameter to detect the beginning and propagation of the oxo-degradation reaction through the carbonyl index (CI) (Antunes et al., 2018). Figure 3 presents the behaviour of the CI of pure copolymer and the prepared formulations under photo degradation and thermal degradation. Figure 3 (a) shows the evolution of CI in pure copolymer and prepared blends during 28 days of test. It is also observed that the CI of C, CM1 and CM2 is near to zero and constant until day 14, then, a little increase is observed from day 14 to day 28. In contrast, copolymers in presence of iron present an important increase of CI during the entire test, which is higher when iron concentration increases. The accelerated increase of CI with the concentration of iron stearate could be explained through the carbonyl groups formation as products of oxidation reaction (Celina, 2013). This fact demonstrates the efficiency of iron to promote degradation of polymers, thus accelerating the scission of peroxides and hydro peroxides during the process. Besides, it could be observed that iron is better than manganese to accelerate the photo oxidation of these molecules. Similar results have been obtained in previous works (Ammala et al., 2011).

Figure 3 (b) presents the increase of CI during the 170 days of the thermal oxidation test. Under these conditions, it is observed that the presence of metal ions enhance the oxidation of the polymer molecule, but it is evident that the manganese is better than iron under temperature to accelerate the oxo-degradation. However, the time required to degradation of samples under temperature is higher than the time required under photo oxidation test.

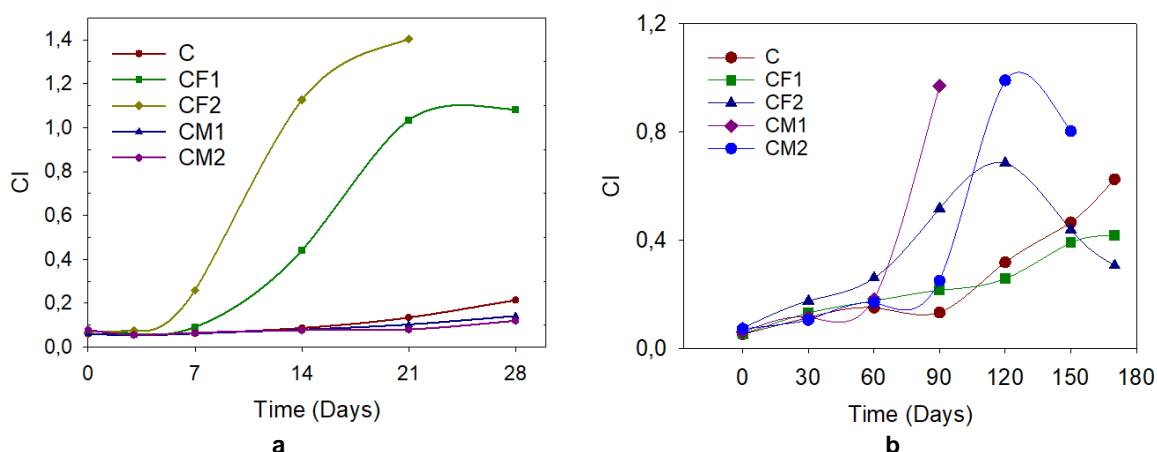


Figure 3: Variation of CI with time for pure copolymer ethylene – norbornene and its blends with iron and manganese stearates: (a) photo-degradation samples and (b) thermal-degradation samples

Figure 4 shows the mechanical behaviour of the prepared formulations under photo-oxidative conditions. Figure 4 (a) shows the variation of the tensile strength of each sample with test time. According to statistical analysis the neat cycloolefin copolymer does not suffer significant changes during the test. This is congruent with the obtained results of FTIR and CI variation with exposition time to photo-oxidation. In the FTIR spectra, the sample C presented no increase in the carbonyl peak at  $1,712\text{ cm}^{-1}$ , this is reflected on CI value, which is practically constant during the 28 days of the test. Similarly, the samples that present changes with time were those containing iron. The changes were statistically significant since the day 14 for CF1 and from day 7 for CF2. This fact could be explained through the molecular cleavage due to the degradative process (Maryudi. et al., 2013). It can also be observed that CF2 lost properties in less time and in a greater proportion than CF1.

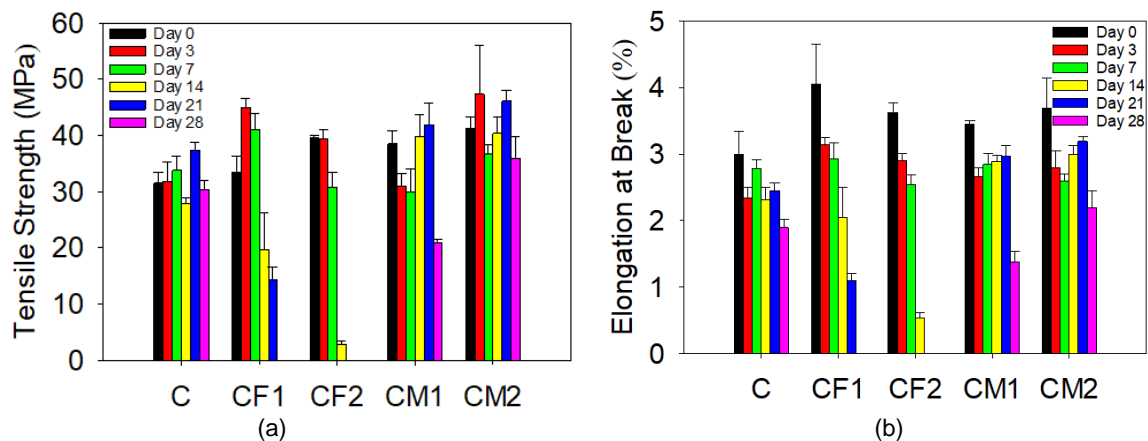


Figure 4: Variation of mechanical tensile properties with exposition time to photo oxidation of pure copolymer and its blends with metal stearates: (a) tensile strength and (b) elongation at break.

Figure 4 b presents the change of elongation at break of samples under photo degradation. As the Tukey test shows, C, CM1 and CM2 samples, there are no important changes with time until day 21. The diminishing elongation capacity is associated with the loss of molecular weight due to molecular cleavage (Islam et al., 2011).

Figure 5 presents the mechanical behaviour of the prepared formulations under thermo-oxidative conditions. The change of tensile strength and elongation at break with time exposition has the same tendency of the samples under UV radiations. Those samples with metal ions content lose properties in less time than the pure copolymer. However, manganese stearate has the highest efficiency to promote thermal oxidation and in its presence the samples lose stability at 60 or 90 days. Mechanical properties could not be measured after 90 days for CM1 and 60 days for CM2, due to the damage of the samples.

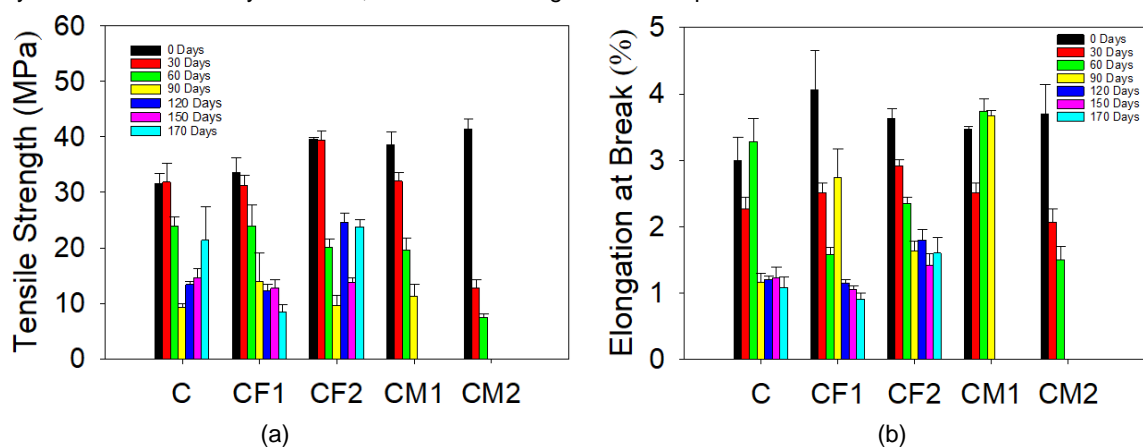


Figure 5: Variation of mechanical tensile properties with exposition time to thermal oxidation of pure copolymer and its blends with metal stearates: (a) tensile strength and (b) elongation at break.

Under thermal conditions, some samples such as C exhibit a minimum tensile strength during some time of the test and then increase. This behaviour could be explained taking in account the reaction mechanism of the degradation reaction and how it could be affected by the intervention of pro-oxidants. The degradation mechanism could cause molecular scission (Ammala et al., 2011) or could produce bonds between chains, thus generating a kind of network (Salem, 2001). Both ways could be possible during the process and the generated structure in each case have opposite behaviour. The loss of molecular weight causes a decrease in mechanical strength, while crosslinks increase stiffness and tensile strength. It is not possible make conclusions about these results because it requires to study the reaction mechanism of this specific degradation reaction.

#### 4. Conclusions

The metal stearates used as pro-degradant agents for ethylene norborneno copolymer accelerate the oxo-degradation reaction, which can be observed in the appearance and growth of a carbonyl signal in the FTIR spectra, the increase of CI and the decrease of the mechanical performance.

The photo oxidation is more aggressive than thermal oxidation, which is evidenced by the fact that photo-degradation requires a third part of the time of thermal degradation to produce a higher increase of CI.

Iron ions are more effective to promote photo-oxidation while manganese ions are better in thermal oxidation.

#### Reference

- Ali, S. S., Qazi, I. A., Arshad, M., Khan, Z., Voice, T. C., & Mehmood, C. T. (2016). Photocatalytic degradation of low density polyethylene (LDPE) films using titania nanotubes. *Environmental Nanotechnology, Monitoring and Management*, 5, 44–53.
- Ammala, A., Bateman, S., Dean, K., Petinakis, E., Sangwan, P., Wong, S., Yuan, Q., Yu, L., Patrick, C., & Leong, K. H. (2011). An overview of degradable and biodegradable polyolefins. In *Progress in Polymer Science (Oxford)* (Vol. 36, Issue 8). Elsevier Ltd.
- Antunes, M. C., Agnelli, J. A. M., Babetto, A. S., Bonse, B. C., & Bettini, S. H. P. (2018). Correlating different techniques in the thermooxidative degradation monitoring of high-density polyethylene containing pro-degradant and antioxidants. *Polymer Testing*, 69(May), 182–187.
- Arndt-rosenau, M., & Beulich, I. (1999). *Microstructure of Ethene / Norbornene Copolymers* †. 32(22).
- Celina, M. C. (2013). Review of polymer oxidation and its relationship with materials performance and lifetime prediction. *Polymer Degradation and Stability*, 98(12), 2419–2429.
- Chiellini, E., Corti, A., D'Antone, S., & Baciú, R. (2006). Oxo-biodegradable carbon backbone polymers - Oxidative degradation of polyethylene under accelerated test conditions. *Polymer Degradation and Stability*, 91(11), 2739–2747.
- Cichosz, S., Masek, A., & Wolski, K. (2019). Innovative cellulose fibres reinforced ethylene-norbornene copolymer composites of an increased degradation potential. *Polymer Degradation and Stability*, 159, 174–183.
- Dixit, S., Dixit, G., & Verma, V. (2016). Thermal degradation of polyethylene waste and jute fiber in oxidative environment and recovery of oil containing phytol and free fatty acids. *Fuel*, 179, 368–375.
- Gutiérrez-Villarreal, M. H., & Zavala-Betancourt, S. A. (2014). Thermo-Oxidative Stability of Cyclic Olefin Copolymers in the Presence of Fe, Co and Mn Stearates as Pro-Degradant Additives. *Polymer - Plastics Technology and Engineering*, 53(17), 1804–1810.
- Islam, N. Z. M., Othman, N., Ahmad, Z., & Ismail, H. (2011). Effect of pro-degradant additive on photo-oxidative aging of polypropylene film. *Sains Malaysiana*, 40(7), 803–808.
- Lago, W. S. R., Aymes-Chodur, C., Ahoussou, A. P., & Yagoubi, N. (2017). Physico-chemical ageing of ethylene–norbornene copolymers: a review. *Journal of Materials Science*, 52(11), 6879–6904.
- Liu, M. O., Lin, H. F., Yang, M. C., Lai, M. J., Chang, C. C., Shiao, P. L., Chen, I. M., & Chen, J. Y. (2007). Thermal, dynamic mechanical and rheological properties of metallocene-catalyzed cycloolefin copolymers (mCOCs) with high glass transition temperature. *Materials Letters*, 61(2), 457–462.
- Maryudi., Hisyam, A., Yunus, R., & Bag, M. (2013). Thermo-oxidative Degradation of High Density Polyethylene Containing Manganese Laurate. *International Journal of Engineering Research and Applications (IJERA)*, 3(2), 1156–1165.
- Roy, P. K., Surekha, P., Rajagopa, C., & Choudhary, V. (2007). Thermal degradation studies of LDPE containing cobalt stearate as pro-oxidant. *Express Polymer Letters*, 1(4), 208–216.
- Roy, P. K., Surekha, P., Raman, R., & Rajagopal, C. (2009). Investigating the role of metal oxidation state on the degradation behaviour of LDPE. *Polymer Degradation and Stability*, 94(7), 1033–1039.
- Salem, M. A. (2001). Mechanical Properties of UV-Irradiated Low-Density Polyethylene Films Formulated With Carbon Black and Titanium Dioxide. *Egypt. J. Sol*, 24(2), 141–150.
- Schmid, C., Cozzarini, L., & Zambello, E. (2020). Microplastic 's story. *Marine Pollution Bulletin*, September, 111820.
- Selke, S., Auras, R., Nguyen, T. A., Castro Aguirre, E., Cheruvathur, R., & Liu, Y. (2015). Evaluation of biodegradation-promoting additives for plastics. *Environmental Science and Technology*, 49(6), 3769–3777.
- Singh, B., & Sharma, N. (2008). Mechanistic implications of plastic degradation. *Polymer Degradation and Stability*, 93(3), 561–584.