

ATR-FTIR SPECTROMETRY CHARACTERISATION OF POLYMERIC MATERIALS

L. BARBEȘ¹, C. RĂDULESCU², C. STIHI²

¹“Ovidius” University of Constanta, 124, Mamaia Bd., 90052, Constanta, Romania,
lbarbes@univ-ovidius.ro; lucille.barbes2009@gmail.com

²“Valahia” University of Târgoviste, 18-24 Unirii Street, 130082, Târgoviste, Romania,
E-mail: radulescucristiana@yahoo.com; cstihi@yahoo.com

Received July 25, 2013

Abstract. The qualitative study on the efficiency of anti-caking and antioxidant additives as long-term thermal stabilizers for polypropylene (PP) using ATR-FTIR spectrometry is reported. Different kinds of additives are used in polymeric materials both for processing, for long-term stabilization and to prevent deterioration of the plastics performance. ATR-FTIR technique is one of the most important spectrometric methods for the quantification and identification of oxidation process in polymeric materials. This technique penetrates in a thin layer of the sample and measures the carbonyl group formation on the surface of the material. The additive-free and additive PP samples (12 cm × 6 cm × 0.5 mm) containing at 1%, 2% and 3% w/w synthetic antioxidant Irganox 1010 (Ciba) and anti-caking calcium stearate, respectively, have been periodically analyzed in 4000 – 750 cm⁻¹ range by IR Affinity -1, Shimadzu FT-IR instrument during six months. These samples were exposed to natural weathering for six months and in this time their chemical structure is monitored. The recorded FT-IR spectra were evaluated according to the carbonyl index. The additive-free PP samples were damaged very rapidly. In the same time PP samples stabilized with Irganox 1010 were deteriorated more slowly, significantly after 150 days.

Key words: polymeric materials, ATR-FTIR technique, additive, long-term thermal stabilization.

1. INTRODUCTION

The performed attenuated total reflectance (ATR) in combination with infrared spectrometry using a Fourier transform (FT-IR) were developed and validated in the last years, for rapid and competitive analysis of native or recycled polymeric materials.

Plastics provide a significant role in our life, contribute to a continuous energy saving and to a sustainable development. In this order it is require the manufacture of a wide variety of products with low cost and excellent

performance. Polypropylene (PP) has become one of the largest polymers in use, because of its low price, excellent mechanical and physico-chemical properties, convenient in process and it have proved the versatility and applicability in wide markets. PP demand in Romania has been continuously growing during the past decade, reaching a total demand volume of 40.000 tonnes in 2010 [1]. However, due to its low surface energy and relatively high crystallinity, the polypropylene derivatives are difficult to use in many applications where biocompatibility and hydrophilicity properties are required.

In general, polymeric materials suffer different chemical degradative reactions in each step of their life cycle that induce alterations in the polymeric chains by chain scission, crosslinking and formation of new functional groups. Also, these degradative processes are responsible of the reduction of the PP long-term stability and a loss of the mechanical properties. Furthermore, plastics may come in contact with a lot of impurities from the surrounding environment and their performances are considerably reduced [2–5].

Polypropylene is slightly more susceptible to attack by strong oxidizing agents than polyethylene or other polymers. A major advantage of polypropylene is to resistance at higher temperature, this makes PP particularly suitable for different application such as medical instruments and it have to be sterilized frequently for use in a clinical environment. Many kinds of phenolic and phosphorous compounds such as Irganox, Irgafos or Hostanox have been used to improve antioxidant properties of PP stability [6–8].

The quantitative characterization of the additives efficiently, and also, the evaluation of antioxidative PP stability using ATR-FTIR spectrometry will become routine analyses [9–12]. Most of the studies have however focused on rheological and mechanical properties of native or recycled polymeric materials, so further investigation about the degradative effects at a molecular scale would be needed [13].

Several analytical techniques were improved to evaluate the stabilization effectiveness of the additives. Different strategies to determine degradation effects include analysis of the changes in chemical functional groups (using vibrational spectrometry or nuclear magnetic resonance), crystallinity and thermal properties (using thermal analysis), morphology (using electron microscopy), mechanical properties (mechanical testing), and molecular weight distribution and composition (using size exclusion chromatography and mass spectroscopic techniques) can be considered to investigate the degree of polymer degradation, depending on the changes at a macroscopic or microscopic scale. Selection of the appropriate sampling method and sample preparation is critical to achieving good results. Polymer samples can take a number of forms, as shown in Table 1 [14].

In the present, the ATR is the most widely used FTIR sampling tool, is more rapid and gives all necessary information about different functional groups transformation on the polymeric structure. In ATR technique, the sample is pressed

against a diamond, zinc selenide or germanium crystal and the absorption of the evanescent wave is measured. Diffuse reflectance (DRIFT) has been widely used in the past for polymers analysis, and remains a useful technique where the sample is physically too large to measure with ATR and a sample can be taken by abrasion.

Table 1

Sampling techniques for FT-IR spectrometry of polymeric materials

Sample form	Suitable techniques
Fine powders (< 2 μm)	ATR; DRIFT; Transmission (KBr)
Irregular shapes, pellets	ATR, DRIFT (abrasive sampling)
Flat, reflective surfaces	ATR, DRIFT (abrasive sampling); Specular reflectance
Single fibers	ATR (diamond); FT-IR microscope
Polymer soluble in volatile solvents	Transmission (cast film)
Thin films (< 25 μm)	Transmission
Large items	DRIFT (abrasive sampling)

The detection and quantification of specific functional groups using ATR-FTIR can be used as a valuable parameter to evaluate the degree of degradation of all plastics that are usually employed in polymer production quality control and are potential techniques for online quality analysis in recycling plants [15–16].

The ATR technique allows analysis of small quantities of samples and without sample preparation, which greatly speeds sample analysis. The principal benefit of ATR sampling comes from the very thin sampling pathlength and depth of penetration of the IR beam into the sample. However, simply placing the thick sample on the ATR crystal and applying pressure generates a nearly perfect result. The total analysis time for the thick polymer by ATR technique is less than 1 minute. With ATR sampling we direct the IR beam into a crystal of relatively higher refractive index. The IR beam reflects from the internal surface of the crystal and creates an evanescent wave, which projects orthogonally into the sample in intimate contact with the ATR crystal. Some of the energy of the evanescent wave is absorbed by the sample and the reflected radiation (some now absorbed by the sample) is returned to the detector. A single reflection ATR system and the multiple reflection ATR system are shown in Fig. 1.

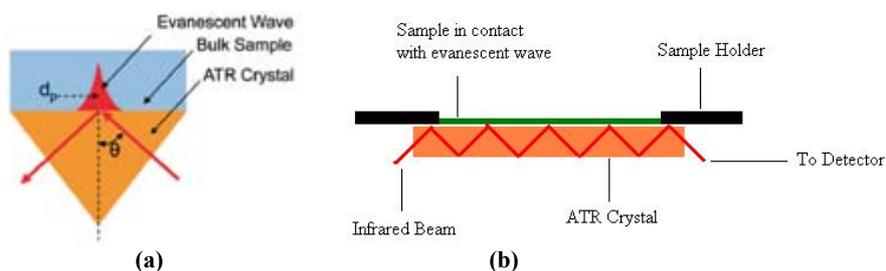


Fig. 1 – Graphical representation of: a) a single reflection ATR; b) a multiple reflection ATR system.

While the analysis of samples by ATR is easy, it is interesting and useful to be aware of each of the experimental factors and how they affect the final spectrum. The most important factors are:

- Refractive indices of the ATR crystal and the sample, which is possible to calculate by the equation (1):

$$\theta_c = \sin^{-1} \left(\frac{n_2}{n_1} \right), \quad (1)$$

where: θ_c is the critical angle; n_2 is the refractive index of the sample; n_1 is the refractive index of the crystal;

- Angle of incidence of the IR beam;
- Critical angle (when we exceed it will observe a purely ATR spectral result);
- Depth of penetration (d_p is defined as the distance required for the electric field amplitude to fall to e^{-1} of its value at the surface, from 0.5 microns up to 5 microns and is defined by equation 2:

$$d_p = \frac{\lambda}{2\pi(n_1^2 \sin^2 \Theta - n_2^2)^{\frac{1}{2}}}, \quad (2)$$

where: λ is the wavelength of light; θ is the angle of incidence of the IR beam relative to a perpendicular from the surface of the crystal;

- Wavelength of the IR beam;
- Effective pathlength – EPL (if we wish to compare the sample absorbance of the ATR measurement with that of a transmission measurement, we need to calculate the volume of the evanescent wave, known as the effective penetration of the IR beam);
- Number of reflections;
- Quality of the sample contact with ATR crystal;
- ATR crystal characteristics.

Quality of sample contact with the ATR crystal is not generally a disadvantage for polymeric samples. For rigid, irregular shaped or porous samples, high pressure sufficient to deform the sample will increase the extent of sample contact and thereby increase sample absorbance [17–19].

This article presents the importance of ATR technique in combination with FTIR spectrometry for stability performances of additive polypropylene samples by calcium stearate and Irganox 1010. The study focused to the monitoring of additive-free and additive polypropylene samples at different concentrations of additives, after exposition under environmental conditions (in soil, seawater and sunlight exposition). Also, assessment of carbonyl index (CI) of additive polymer samples was realised.

2. MATERIALS AND METHODS

2.1. SAMPLES

Samples of commercial additive free – polypropylene (**af-PP**) with following characteristics: fine powder with molecular weight: $M_w = 174,000$ g/mol; $M_w/M_n = 2.32$; density: 0.905 ± 0.917 g/cm³ and the melt flow index: 0.8 ± 1.4 g/10 min, and additive polypropylene were used.

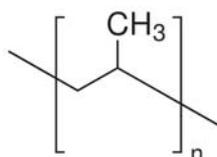


Fig. 2 – Chemical and molecular structure of PP.

Two types of additive polypropylene containing 1%, 2% and 3% w/w Irganox 1010 (Ciba-antioxidant agent) – **i1010-PP** and calcium stearate (anti-caking agent) – **cs-PP** were studied.

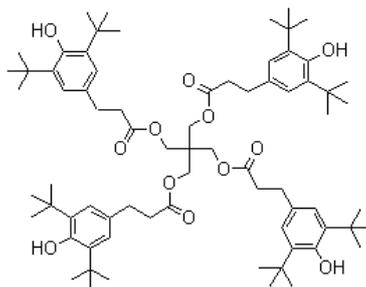


Fig. 3 – Chemical structure of antioxidant Irganox 1010.

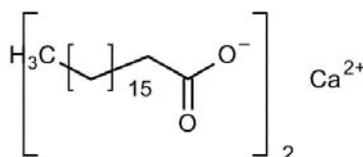


Fig. 4 – Chemical structure of anti-caking agent Ca stearate.

2.2. SAMPLES PREPARATION

The PP samples were made in the Petrochemicals laboratory using the compression process at the melting temperature of the thermoplastic material in a limited cavity. There have been three different sample set. Each set contains

twenty-one specimens of rectangular film plates with the same geometrical characteristics: L-12 cm, l- 6 cm and thickness – 2 mm.

It was necessary to use the following materials: minimum 2 g of PP fine powder, 100÷300 mg additives/kg polypropylene powder, frames, backing plate, melinex foils and the following apparatus: Carver Press and Ray Ran injection device. The main processes to produce polypropylene plates are compression molding and injection molding. Most compression molding method starts with a powder compound. The quantity of polypropylene powder is fed into a heated mold which the compound will flow and fill the mould capacity. If a thermoplastic binder is used, the mold has to be cooled to a temperature below the melting temperature before the plate can be removed.

2.3. ATR-FTIR SPECTROMETER CHARACTERISTICS

ATR-FTIR technique was used for additive free – PP and additive – PP samples analysis in the wavenumber range of 4000–750 cm^{-1} to gives out the indication of formation of the oxidation products by using IRAffinity – 1 spectrometer, Shimadzu instrument. The instrument specifications are shown in Table 2. ATR accessory equipped with a single reflection diamond ATR crystal on ZnSe plate was used for all of the analysis.

Table 2

Characteristics of IRAffinity – 1 Shimadzu spectrometer's components

COMPONENT	CHARACTERISTIC
Interferometer	Michelson interferometer (30 ⁰ incident angle)
Optical system	Single-beam optics
Beam splitter	Germanium-coated KBr
Light source	High-energy ceramic light source
Detector	DLATGS detector equipped with temperature control mechanism
Wave number range	7,800 to 350 cm^{-1}
Resolution	0,5; 1; 2; 4; 8 or 16 cm^{-1}
S/N ratio	30,000:1 (peak-to-peak, 4 cm^{-1} resolution, in a neighborhood of 2,100 cm^{-1})
Mirror speed	4-step selection of 2.0, 2.8, 5, or 9°mm/sec
Data sampling	He-Ne laser
Gain	Automatic or manual setting ($\times 1$ to $\times 128$)

2.4. EXPOSURE CONDITIONS AND PROCEDURE

The all polypropylene samples were exposed to natural weathering (all environmental effects such as rain, sunlight, wind etc.) at Constanta district. The natural exposure was conducted for a period of 5 months from August 2012 to

February 2013. The climate in the region is affected by continental and maritime influences due to the Black Sea. The summers are dry and hot and the winters are cold. According to the data published by National Meteorological Administration of Romanian Ministry of Environment and Forests the annual average temperature lies around 11.1° C and the annual precipitation in 2012 was 388 mm [20–21]. The dominant soil types from Constanta district area were formed and evolved mostly on loess and are represented by calcic and calcareo-calcic chernozem. The specimens were attached to a rack holder and were placed on the research zones.

Samples were collected weekly. ATR- FTIR spectral analysis before and after the exposure on the surface of specimens were carried out to study effect of natural weathering.

In accordance with the last requirements, soil and seawater samples were characterized in the research area. The physical and chemical parameters were analyzed:

- seawater samples– pH [units], conductivity [$\mu\text{S}/\text{cm}$], SO_4^{2-} [g/L], Cl^- [mg/L] and oxidability [mg/L];
- soil samples – pH [units], humidity [%], ash [%], total hydrocarbons [mg/kg], total nitrogen [%], SO_4^{2-} [g/L], Cl^- [mg/L].

2.5. ESTIMATION OF CARBONYL INDEX

Carbonyl Index (CI) in this work was calculated using equation (3).

$$\text{CI} = \frac{A_{1775(1715)}}{A_{2870}}, \quad (3)$$

where: $A_{1775(1715)}$ – absorbance of carbonyl group (-CO-); A_{2870} – absorbance of methylene group (-CH₂-), symmetric stretching vibration.

3. RESULTS AND DISCUSSION

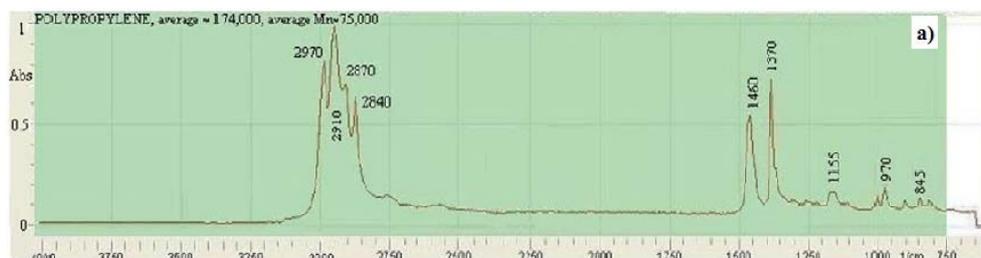
The ATR-FTIR spectra for **af-PP**, **calcium stearate** and **Irganox 1010** powders are shown in Fig. 6.

af-PP spectra (Fig. 6a) indicated the following main assignments and peaks for specific functional group: ν_{as} (methyl group -CH₃) – 2970 cm^{-1} (*i*); ν_{s} (-CH₃) – 2910 cm^{-1} , (*i*); ν_{as} (methylene group - CH₂ -) – 2870 cm^{-1} (*m*); ν_{s} (- CH₂ -) – 2840 cm^{-1} , (*m*); δ_{as} (-CH₂-) – 1460 cm^{-1} , (*m*); δ_{s} (-CH₃) - 1370 cm^{-1} , (*i*).

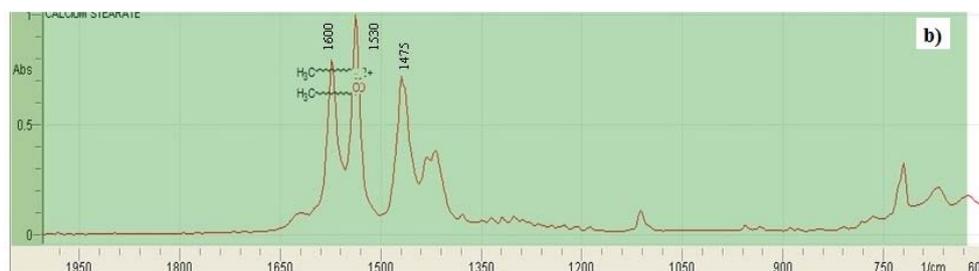
Calcium stearate spectra (Fig.6b) shows the principal following data: ν_{as} (methyl group -CH₃) – 1600 cm^{-1} (*i*); ν_{s} (-CH₃) – 1530 cm^{-1} (*i*); δ_{s} (-CH₂-) - 1475, (*m*).

Irganox 1010 spectra (Fig. 6c) indicated the following peaks for its corresponding functional group: ν_{s} (carbonyl group >C=O) – 1735 cm^{-1} (*i*); ν_{as} (-C-

O-C-) – 1275 cm^{-1} (*m*); $\delta_{\text{as}}(-\text{C-H})$ – 1140 cm^{-1} (*i*); $\nu_{\text{s}}(-\text{C-O-C-})$ – 1040 cm^{-1} , (*m*); $\delta_{\text{s}}(-\text{C-H})$ – 765 cm^{-1} , (*m*).



a)



b)



c)

Fig. 6 – a) – af-PP ATR-FTIR spectra; b) – calcium stearate ATR-FTIR spectra; c) – Irganox 1010 ATR-FTIR spectra.

Formation or disappearance of functional groups in the additive free and additive polymers during the process of degradation can be successfully monitored by ATR – FTIR spectrometry. The main focus was on the carbonyl group region present between 1700 and 1800 cm^{-1} . The changes in the relative absorbance intensity of ketone group (corresponding to 1775 cm^{-1} for **cs** – **PP** samples or 1715 cm^{-1} for **i1010** – **PP** samples) to that of methylene group (at 2870 cm^{-1}) were monitored during the degradation process. The ATR-FTIR spectra for stabilized polypropylene by 1% w/w calcium stearate before and after exposure to natural weathering, with significant example for each, is shown in Fig. 7a, b and c.

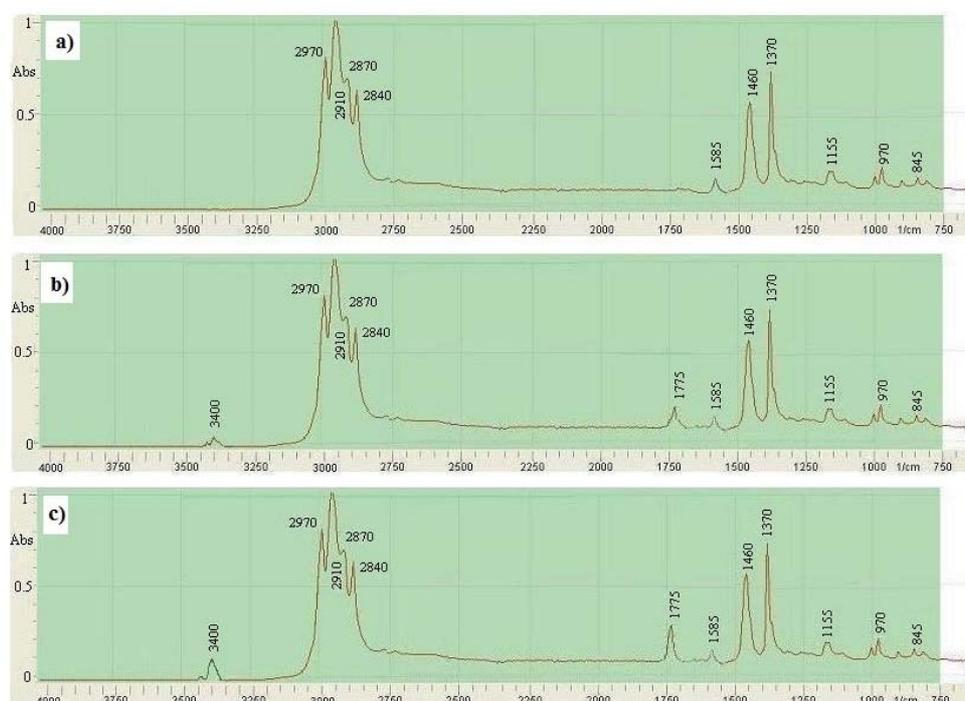


Fig. 7 – 1% w/w cs – PP spectra: a) – before exposure; b) after 7 days exposure to natural weathering; c) after 2 months exposure to natural weathering.

The ATR-FTIR spectra for stabilized polypropylene by 3% w/w Irganox 1010 before and after exposure to natural weathering, with significant example for each, is shown in Fig. 8.

Before exposure to natural weathering, in **cs - PP** spectra show carboxylate bands at 1585 cm^{-1} at equal intensity in the powder form and the polymeric films. This showed the calcium ions remains associated with the COO^- ions in both structures, in powders and films, respectively.

Eq. 3 is used to calculate the ketone group indices of the PP samples. The absorbance intensity value corresponding to methylene group bending was used as the standard, since it was considered to remain unchanged during the period of study. The $1700\text{--}1800\text{ cm}^{-1}$ region in IR spectra indicates the presence of oxidized groups. Peaks at 1775 cm^{-1} (or 1715 cm^{-1}) corresponding to the modification of carbonyl groups were observed after exposure samples to natural weathering which are indicated a oxidation process of the polymer. These peaks either became more strong and sharp or disappeared by the end of sixth months. The carbonyl indices were calculated from these spectra and the results are shown in: Fig. 9 – sunlight exposure, Fig. 10 – seawater exposure and Fig. 11 – soil exposure.

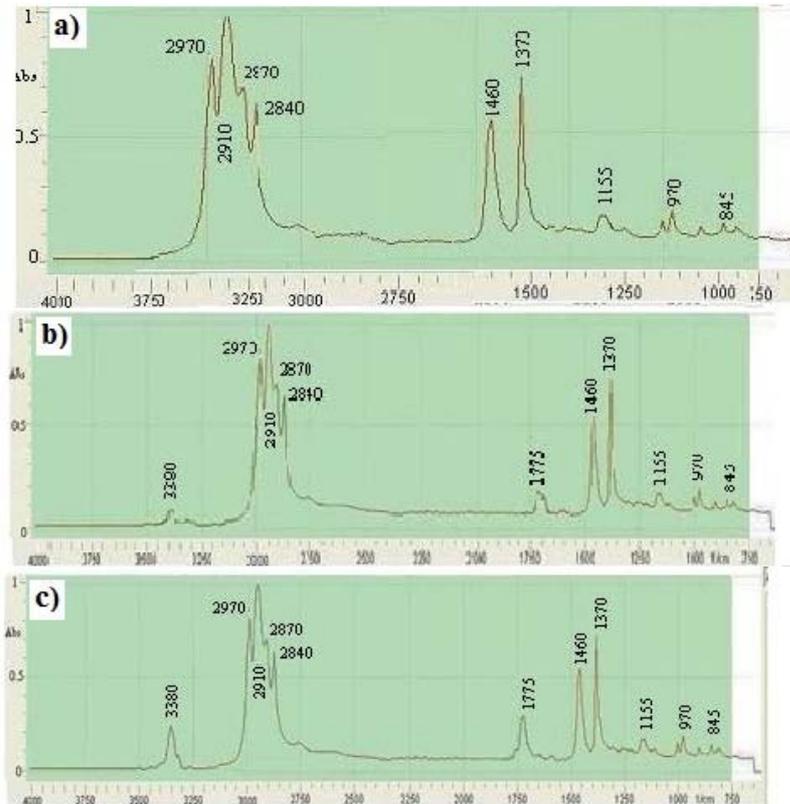


Fig. 8 – 3% w/w i1010 – PP spectra: a) – before exposure; b) after 15 days exposure to natural weathering; c) after 3 months exposure to natural weathering.

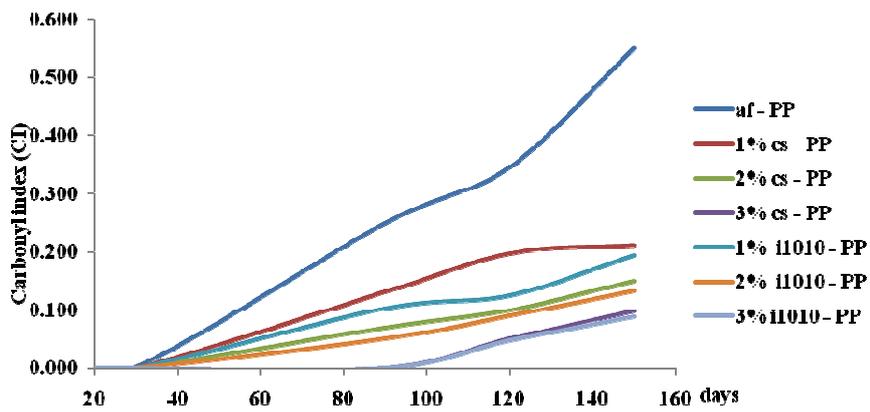


Fig. 9 – Results of af-PP and additive-PP samples at sunlight exposure.

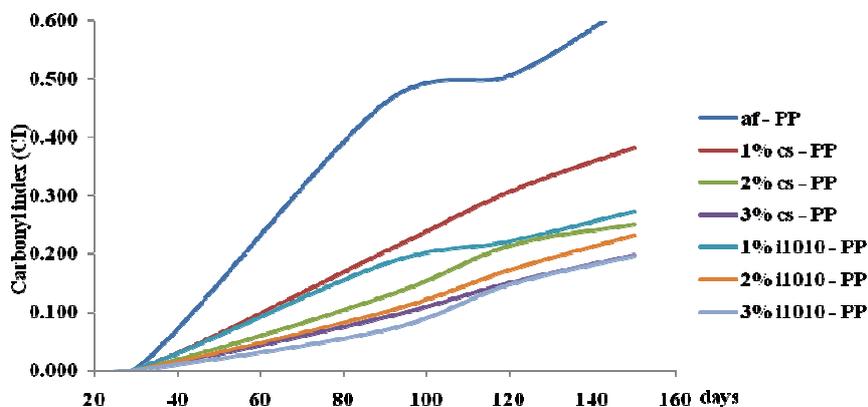


Fig. 10 – Results of af-PP and additive-PP samples in sea water exposure.

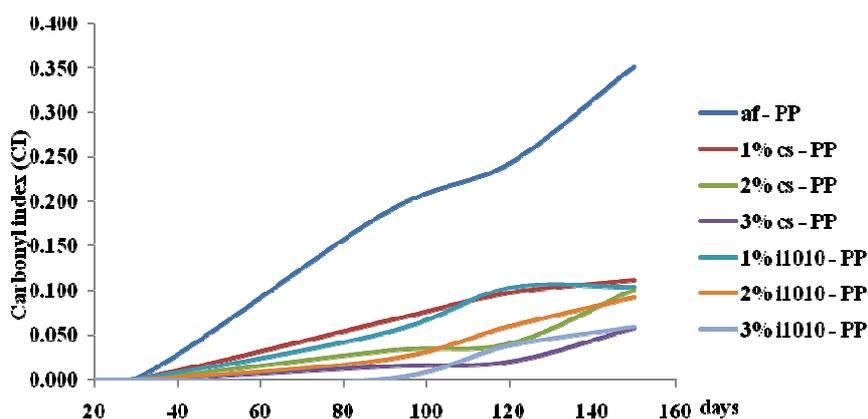


Fig. 11 – Results of af-PP and additive-PP samples in soil exposure.

It can be seen from these figures that the carbonyl index has more grown up for additive-free polymeric films than others, in order: soil < sunlight < seawater exposure. Similar results were obtained for additive polymeric films by the increasing of calcium stearate or Irganox 1010 addition: 1%, 2% or 3% w/w. However, it is interesting to note from the results above, between Irganox 1010 and calcium stearate, the rate of oxidation in the former is less in the seawater exposure than sunlight or soil exposure. This result could be attributed to a higher water-resistant polymer films stabilized with Irganox to those of calcium stearate.

Thus, it is presented that the main role of the phenolic antioxidant is reducing the consumption rate of stabilizers in the multiple oxidation process of polymeric materials.

4. CONCLUSIONS

Based on the results obtained in this work, it can be said that ATR- FTIR spectrometry can be helpful in the examinations of the chemical structure of the polymer surface layer and changes in the layer structure caused by the effects of different natural weathering exposure (sunlight, seawater and soil exposure).

The efficiency use of the 1–3% w/w antioxidant or anti-caking agents (calcium stearate and Irganox 1010) on polypropylene films stabilization was successfully characterized by ATR-FTIR spectrometry. Also, addition of additives in polypropylene powder composition can be easily monitored in different environmental conditions [22–23] in order to appreciate the oxo-degradability of polymeric films.

Carbonyl index, defined as the ratio of carbonyl and methylene absorbance's, was used to express the levels of ketone group analysed in the additive free and additive polypropylene.

Marine environment is found to be one of the major medium for degradation of polymeric films by comparison with exposure at direct sunlight or in soil.

REFERENCES

1. *** <http://www.petrochemicals.ro/online/index.php>
2. T. Muthukumar, A. Aravinthan, D. Mukesh, *Polymer degradation and stability*, **95**, 10, 1988–1993 (2010).
3. T. Ojeda, A. Freitas, K. Birck, E. Dalmolin, R. Jacques, F. Bento, F. Camargo, *Polymer degradation and stability*, **96**, 4, 703–707 (2011).
4. Grigoriadou, K.M. Paraskevopoulos, K. Chrissafis, E. Pavlidou, T.G. Stamkopoulos, D. Bikiaris, *Polymer degradation and stability*, **96**, 1, 151–163 (2011)
5. J.L. Pablos, C. Abrusci, I. Marín, J. López-Marín, F. Catalina, E. Espí, T. Corrales, *Polymer degradation and stability*, **95**, 10, 2057–2064 (2010).
6. N. Nagai, T. Matsunobe, T. Imai, *Polymer degradation and stability*, **88**, 2, 224–233 (2005).
7. Geburtig, V. Wachtendorf, *Polymer degradation and stability*, **95**, 10, 2118–2123 (2010).
8. S Krishna Mohan, T. Srivastava, *J. Biochem. Tech.*, **2**, 4, 210–215 (2010).
9. Jakubowicz, *Polymer Degradation and Stability*, **80**, 39–43 (2003).
10. C. Jin, P.A. Christensen, T.A. Egerton, E.J. Lawson, J.R. White, *Polymer Degradation and Stability*, **91**, 5, 1086–1096 (2006).
11. Ioniță, A-M. Albu, C. Radulescu, *Revista de Chimie*, **64**, 6, 612–619 (2013).
12. Ioniță, A-M. Albu, C. Radulescu, E.I. Moater, V.Gh. Cimpoca, M. Gîrtu, *Journal of Optoelectronics and Advanced Materials*, **10**, 11, 2859–2863 (2008).
13. A. Geburtig, V. Wachtendorf, *Polymer degradation and stability*, **95**, 10, 2118–2123 (2010).
14. W.L. Oliani, D.F. Parra, A.B. Lugo, *Radiation Physics and Chemistry*, **79**, 3, 383–387 (2010).
15. G.E. Luckachan, C.K.S. Pillai, *J. Polym. Environ.*, **19**, 637–676 (2011).
16. C. Hanjia, X. Shi, Y. Zhu, Y. Zhang, J. Xu, *Frontiers of Chemical Engineering in China*, **4**, 3, 336–341 (2010).
17. W. Urbaniak-Domagala, *Advanced Aspects of Spectroscopy*, Editor Muhammad Akhyar Farrukh, Chapter 3, 2012, pp. 85–104.
18. *** http://www.piketech.com/files/pdfs/AnalysisOfPolymersByATR_FTIRspectroscopy_AN.pdf

19. *** <http://www.piketech.com/files/pdfs/ATRAN611.pdf>
20. *** <http://www.meteoromania.ro/anm>
21. A. Bărbulescu, J. Deguenon, *International Journal of Mathematical Models and Methods in Applied Sciences*, **6**, 5, 617–624 (2012).
22. C. Radulescu, C. Stihi, I.V. Popescu, I. Ionita, I. Dulama, A. Chilian, O.R. Bancuta, E.D. Chelarescu, *D. Let, Romanian Reports in Physics*, **65**, 1, 246–260 (2013).
23. I.V. Popescu, M. Frontasyeva, C. Stihi, Gh.V. Cimpoca, C. Radulescu, G. State, A. Gheboianu, C. Oros, O. Cilicov, I. Bancuta, I. Dulama, *Romanian Reports in Physics*, **63**, 1205–1214 (2011).