Structural Analysis of (LDPE) and (HDPE) Films Biodegraded in Sanitary Landfill- II

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Summary: The use of the polymeric commodities LDPE and HDPE in the most varied industrial applications and for economic interests, it produces discards in the waste, and great demand of the same ones in the sanitary landfill. In this work we have studied degradation/biodegradation of the polyethylene (PE) in the landfill São Giácomo in Caxias do Sul, Brazil. The PE was collected in cell C4 with 94 months of age and different depths (11 to 16 m). The samples films was analyzed thermogravimetric (TGA), morphologic (SEM) and structural (FT-IR) determinations of these degraded materials in landfill. The samples in the waste presented the one degradation pick and for the LDPE mass loss it increases and for HDPE mass loss creases with the dump. Evidenced structural changes with absorbency increment corresponding mainly to vibrations in new frequencies. The morphologic analyses (SEM) the films samples they present scales and fissures.

Keywords: biodegradation; degradation; landfill; polymeric commodities

Introduction

The polymerics commodities are is a major component of plastic waste from domestic refuse. The municipal waste São Giacomo, located in the Caxias do Sul-RS/Brazil, according studies carried through in 2002, it evidence the generation of 15% of polymeric residues.[1] The organic matter degradation in urban solid wastes at different conditions, such as anaerobic and aerobic process.[2] The sanitary landfill can be considered as a biological reactor, where there are suitable conditions for the growth of the bacteria that are responsible for biodegradation. Such an analysis can reveal the presence of anaerobic microbial activity, considering that the leachate of cell C4 has predominantly methanogenic characteristics (in 70% of the cases the BOD/COD ratio was below 0.4).[3] The overall decomposition of the organic matter has been assumed to follow four sequential biochemical reactions: hydrolysis, acidogenesis, acetogenesis and methanogeneses.[4] They possess enzymatic arsenals that they are, also, capable to act on synthetic chemical antropogenic substances originating from of the activity.[5] Degradation products patterns and morphology changes are demonstrated to be means by which to differentiate between physical/chemical (abiotic) and biological (biotic) ageing of degradable polymers. There is an strong synergism between biodegradation and environmental factors, and biodegradation can, in practice, never be entirely separated from the purely physical and chemical. Biodegradation is seldom due a single cause, but a combined effect including heat, UV, stress and water.[6] The work was study and presented the thermogravimetric analysis, structural and morphologic determinations of these LDPE and HDPE films in cell C4 for sanitary landfill in the different dump.

Experimental

The LDPE and HDPE samples were collected by perfurations carried in the landfill

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cells C4 and at depths of 11 to 16 m. The structural analyses for spectrocospy for FT-IR, model Impact 400, Nicolet, with washed films, according to norm ASTM D 6288-98, to testing and swollen in dichlorine methane on KBr. The thickness of the films was of 30–50 μm. The thermogravimetric analyses (TGA) of sample was performed on a Shimadzu, TGA-50, in N_2 atmosphere, flow 100 $mL \cdot min^{-1}$ from 25 to 900 °C and the samples with approximately 100 mg were used for the experiments. The surface of the samples were covered with gold in a diode-sputtering Baltec SCD050 coater and observed in a JEOL JSM 5800 scanning electron microscope (SEM) at accelerating of 20 kv.

Results and Discussion

The structural analyses for spectroscopy for FT-IR for LDPE and HDPE showed in Figure 1 and 2.

The LDPE films were compared with virgin sample showed formation of new absorbances in the FT-IR region 1729, 1611, 1031 and 966 cm^{-1}. The formation of carbonyl groups is increases by photoxidation, but also by increasing stress even after storage in an abiotic environment[7] and when carbonyl groups have been produced these are attacked by microorganisms which degrade the shorter fragments of polyethylene chains to the end products.[8] The appearance of the band in the 966 cm^{-1} in the cell C4 - 94 months for age, can be related the crystanillity change.[9] The structure de LDPE in the landfill in biotic and abiotic atmosphere, increase in double bonds, presented mechanism Norrish type I and II degradation.[6]

The film HDPE it presents carbonyl group in 1744 cm^{-1} evidencing the ester carboxyl group. The mechanism of degradation of HDPE of the embankment should be associated the scission β in environmental biotic.

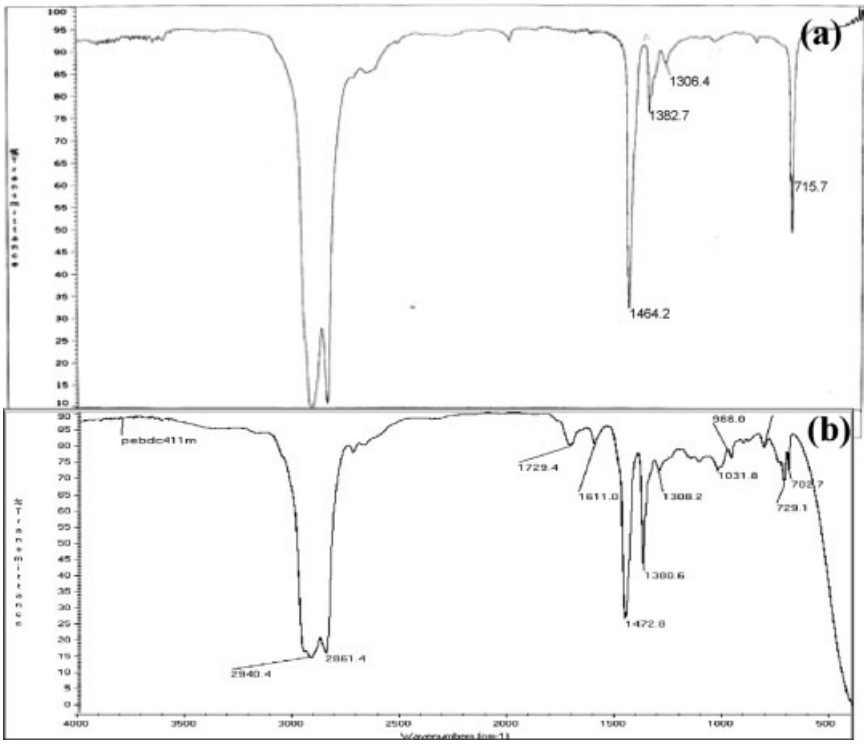

Figure 1.
Spectroscopy for FT-IR the film LDPE (a) virgin and (b) LDPE in the cell C4.

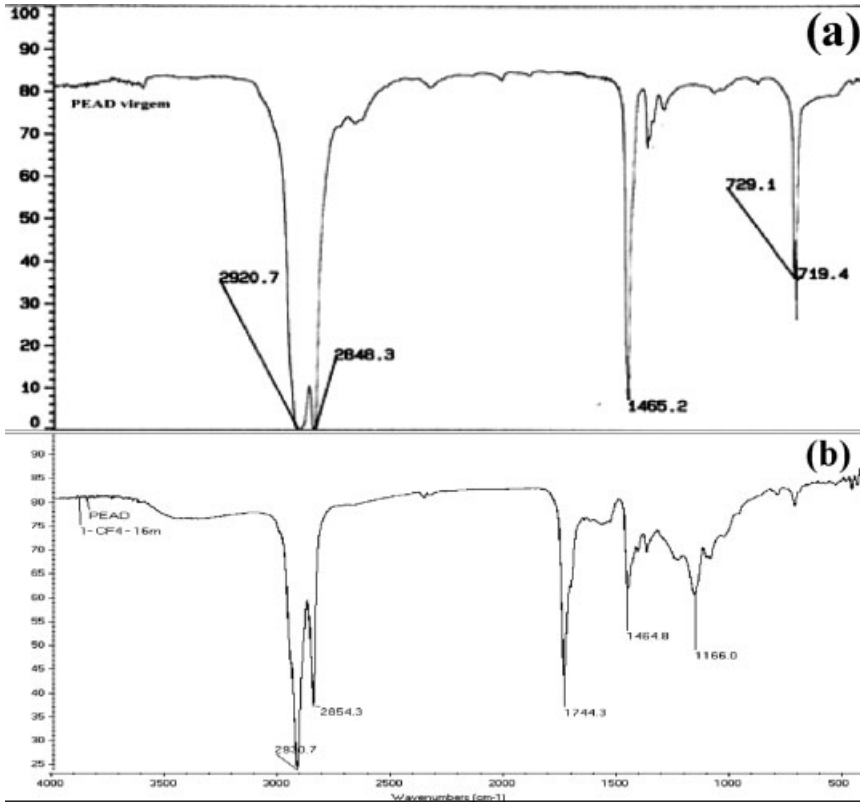

Figure 2.
Spectroscopy for FT-IR the film HDP (a) virgin and (b) HDPE in the cell C4.

The thermogravimetric (TG) the LDPE and HDPE virgin and the samples collected in the municipal waste in the cell C4 with 94 months of age we observed only one mass stage corresponding to the degradation reaction. The maximum degradation temperatures for LDPE virgin and C4-11m suggesting a high thermal stability. The structure of the HDPE is linear, contends few ramifications and amorphous[8] and the LDPE presents little ramified structure smaller force of interaction between molecules, presents structural alterations of degradation, such as scission chain cross-linking , ecc.[7]

Table 1.
Thermogravimetric analysis LDPE and HDPE (10 °C/min in N_2).

Polymer	Temperature (°C)	Weight Loss (%)
LDPE virgin	483,5	98,75
LDPE		
C4 – 11 m	488,17	98,7
C4 – 12 m	485,17	98,92
C4 – 16 m	485,16	99,08
HDPE virgin	488	98,66
HDPE		
C4 – 13,5 m	481	94,78
C4 – 16m	488	96,75

The LDPE virgin show small degradation temperature that can be random scission of the chain. SEM micrographs the samples LDPE and HDPE collected in the municipal waste by show disintegration of the surface. The erosion of the surface and fissures can be observed in cell C4 -16m and cell C4 -16m and 94 months of age (Fig. 3).

Conclusion

The abiotic peroxidation initiate biological attack by microorganisms and in the landfill

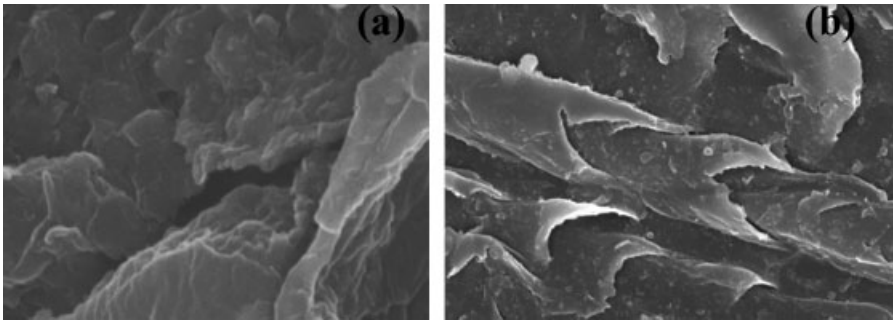

Figure 3.
Micrographs (SEM) of biodegraded films; (a) HDPE cell C4-16 m, and (b) LDPE cell C4- 16 m.

the synthetic hydrocarbon polymers they are biodegrade readily in the presence of a variety of thermophilic microorganism. Surface bioerosion with SEM confirms that microorganisms grow in the surface of the polymer and its presented eroded and disintegrate. For LDPE samples the temperature and weight loss as a function the depth. In the HDPE resulted increasing value can be attribute to structures and morphology changes. The different degradation mechanisms and a decreasing value of crystallinity and lamellar thickness of the LDPE and HDPE films was determinate in environmentally realistic conditions.

Acknowledgements: The authors thank the CNPQ, FAPERGS and Caxias do Sul University for financial support.

[1] A. Zaterra, O. Bianchi, D. Peresin, V. E. Schneider, R.N. Brandalise, M. Zeni, 7° Congresso Brasileiro de Polímeros, Belo Horizonte-MG/Brasil, **2003**.
[2] F. Kerbekus et al. Tratamineto Mecânico -Biológico de Desechos? In: *Proyecto Sectorial "Promocion delTratamiento Mecânico-Biológico de Desechos"*. Alemanha, Edição GTZ **2000**.
[3] A .M. C. Grisa, Tese de Doutorado Universidade de Leon, ES, **2004**.
[4] A. Haarstrick, D. C. Hemple, L. Ostermann, H. Ahrens, D. Dinker, *J. Inter. Solid Waste* **2001**, *19*, 320.
[5] R. F. Vazoller, Microbiologia e Saneamento Ambiental, Tesis USP,BR, **2001**.
[6] A. C. Albertsson, C. S. Anderson, S. Karlssson, *Polym. Degrad. and Stab.* **1987**, *18*, 73.
[7] D. J. Carlsson, D. M. Wiles, *Encyclopedia of Polymer Science and Engineering*, John Wiley & Sons, **1986**, 630–696.
[8] A. C. Albertsson, C. Basrenstedt, S. Karlsson, T. Lindberg, *Polymer* **1995**, *36*, 3075–3083.
[9] J. Gu, *Inter. Biodeterioration & Biodegradation* **2003**, *52*, 69–91.

