Journal of Research in Environmental Science and Toxicology (ISSN: 2315-5698) Vol. 2(7) pp. 126-130, August 2013
DOI: http:/dx.doi.org/10.14303/jrest.2013.077
Available online http://www.interesjournals.org/JREST

Full Length Research Paper

Kinetic parameters for degradation of municipal waste polymer

Ana M. C. Grisa, Janaina S. Crespo and Mara Zeni

Chemistry and Physics Department, Caxias do Sul University (UCS) 95001-370, Caxias do Sul, RS – Brazil

Accepted 14 August, 2012

Low-density polyethylene (LDPE) from the landfill São Giacomo in Caxias do Sul - Brazil was selected for a study on its degradation mechanisms based on its abundance in solid waste. The thermogravimetric analysis and the kinetic parameters, using the Freeman-Carroll method, were obtained for samples collected from different points and depths of the landfill. According to this method, activation energy (*Ea*) decreases with an increase in the waste age and these results suggest structural alterations through degradation and possible changes in the polymeric chemical structure in the ecosystem.

Keywords: Low-density polyethylene, Degradation Kinetic, Thermogravimetric analysis, Landfill.

INTRODUCTION

Municipal landfill sites are complex ecosystems with several transformations based on the fundamental relationships between the physico-chemical parameters, thermodynamics and different microbial processes. The increase in the consumption of thermoplastics worldwide highlights the importance of some polymeric commodities. According to studies carried out in 2002, the municipal landfill site São Giácomo, located in Caxias do Sul, RS, Brazil, generates 15% of polymeric residues (Zattera et al., 2006).

Polymer degradation in landfills is often initiated by the synergistic effect of several degradation mechanisms (Haider and Karlsson, 1999; Duchin and Lange, 1998). The degradation of LDPE proceeds through various slow stages (Kawai et al., 2002). The primary mechanisms responsible for polymer degradation in landfills are thermal, thermal-oxidative, mechanical, photochemical, photo-oxidative and biological.

The purpose of the this study was to investigate the degradation of low density polyethylene collected from the landfill São Giácomo in different cells and at depths of 8 to 16 m.

Thermogravimetric analysis of the LDPE was carried out using the Freeman-Carrol method, with a differential form of the rate equation, in the determination of the kinetic parameters, activation energy and in the evaluation of the stability of polymer commodities (Liu and Fan, 1999).

Experimental

The LDPE samples were collected by perforations carried out at three sample sites in the landfill cells C9, C4 and C3 and at depths of 8 to 16 m. After collection, the material was washed according to the standard method ASTM D 6288-98.

The degradation of samples of plastic waste from domestic refuse was performed with a SHIMADZU TGA-50, in N_2 atmosphere, flow 50 mL min^{-1} and approximately 10 mg samples were used for the experiments. Non-isothermal experiments were performed in the temperature range of 25-900°C at a heating rate of 10°C min^{-1}. The thermogravimetric data were analyzed using the Freeman-Carrol method

*Corresponding Author E-mail: mzandrad@ucs.br

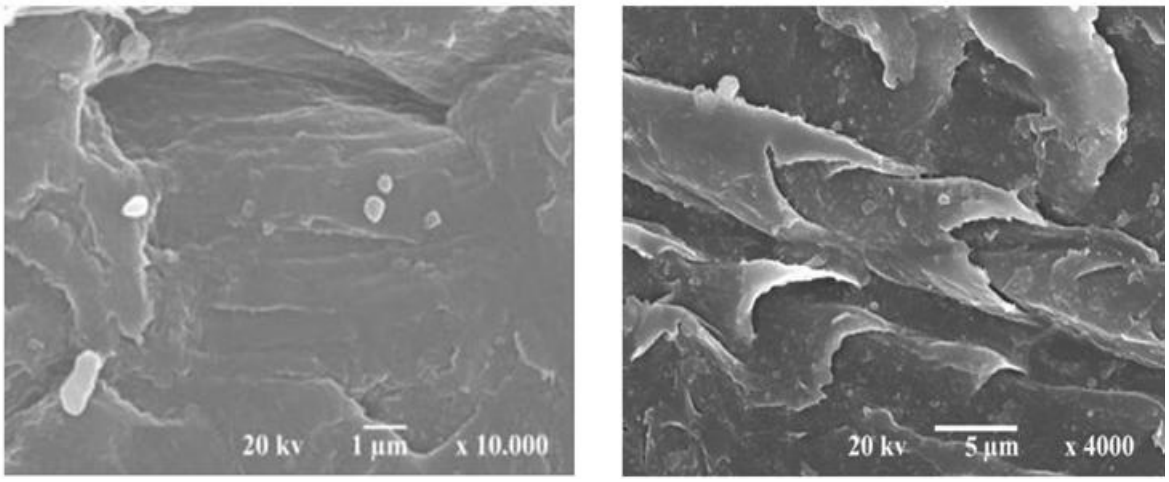

Figure 1. Microscopy (SEM) of LDPE (a) cell C3-10 m and (b) cell C4-16 m.

(Hatakeyama and Quinn, 1994). In the Freeman-Carrol method, the degradation rate taken as weight loss as a function of time is considered to be dependent on temperature and composition. Considering W as the remaining mass fraction in a TG curve that represents thermal degradation at a constant heating rate, and assuming the reaction order to be equal to unity, the degradation reaction can be described by:

$$\ln([-dW/dt]W) = Ea(-1/RT) + \ln A \quad (1)$$

where,

A: pre-exponential factor;

Ea: apparent activation energy;

R: universal constant of gases;

T : absolute temperature.

The slope of the plot of ln([-dW/dt]W) vs-1/RT determines the apparent activation energy and the linear coefficient corresponds to the pre-exponential factor (Viletti et al., 2002).

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 an accelerating voltage of 20 kV.

RESULTS AND DISCUSSION

The morphological analysis of the LDPE films was carried out using scanning electron microscopy for samples taken from cells C3 and C4 (Figure 1). The samples taken from cells C3-10 m and C4-16 m show fissures, erosion of the surface and the presence of bacterial cells.

The thermogravimetric (TG), the derivate (DTG) curves and activation energy (*Ea*) of virgin LDPE and of the sample collected from the sanitary cell C4-16 m obtained with a heating rate of 10°C/min in N_2, are presented in Figures 2 and 3, respectivily. The thermogram of the sample collected from the waste site show only one weight loss stage corresponding to the degradation reaction (i.e. one degradation temperature in the kinetic parameters study). The major processes of degradation were considered according to the DTG temperature. It was observed that the maximum degradation temperatures of the DTG curves for the LDPE samples taken from the same cells at the different depths of the landfill, showed a greater weight loss. The calculations for the activation energy (*Ea*) gave a correlation factor close to unity and Table 1 gives the results obtained for the degradation of the virgin LDPE sample and the samples collected from the landfill site (Poletto et al., 2011).

The application of the Freeman-Carrol method to the thermogravimetric data for the LDPE shows that the virgin sample has two activation energies and the samples collected from the landfill site have just one activation energy.

For the LDPE samples taken from different depths of the landfill the apparent activation energies (*Ea*) decreased as a function of depth which may be due to structural alterations such as chain scission, abiotic oxidation and the presence the smaller chains before degradation. Also, the virgin LDPE showed lower degradation temperatures due to a random scission of the chain (Grisa et al., 2012).

CONCLUSION

Erosion, crack zones at the surface and the presence of the microorganisms were identified during the biodegradation of the LDPE which is responsible for the degradation and loss of some sample properties.

The Freeman-Carroll method is effective in the determination of the activation energy for different

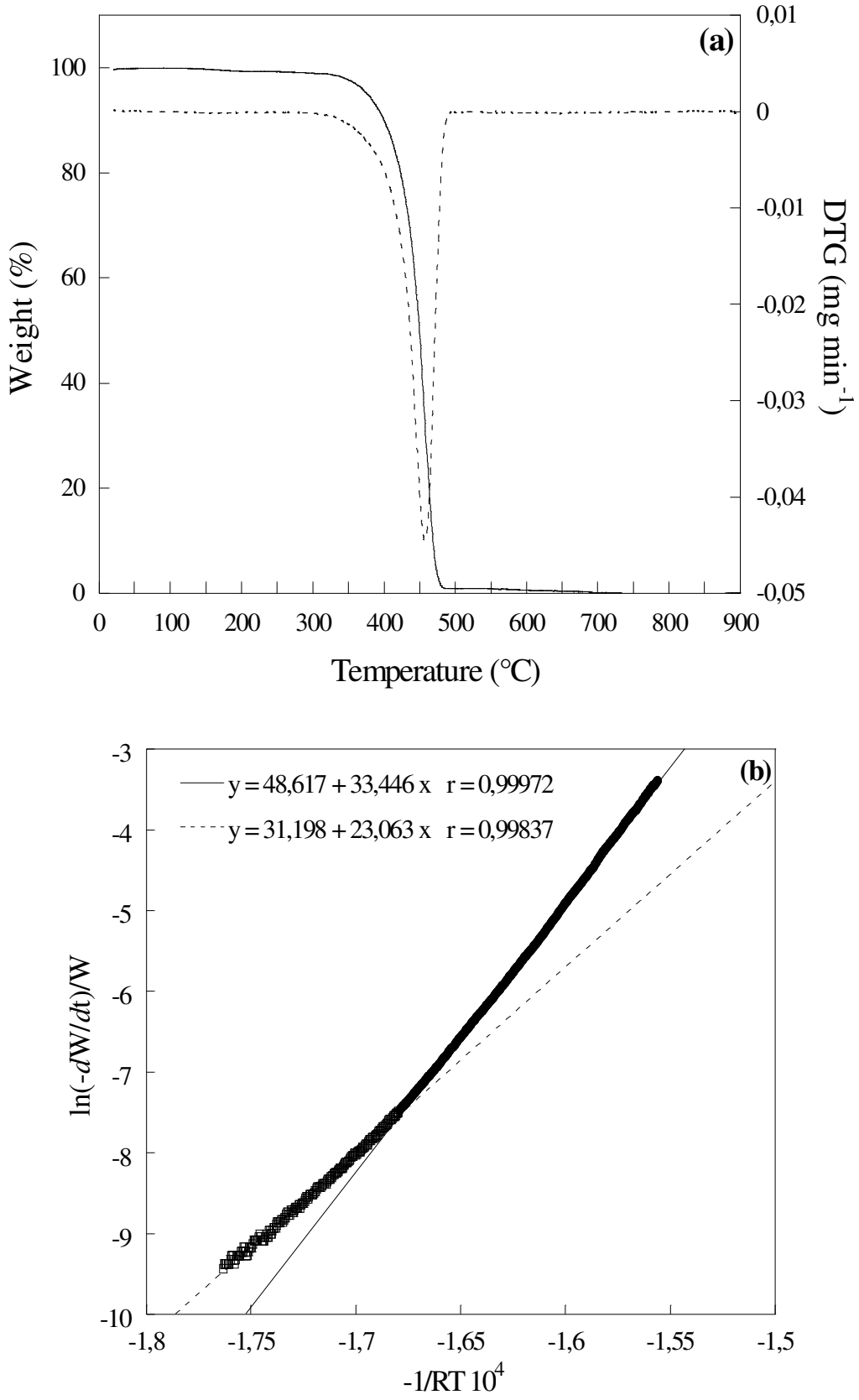

Figure 2. Thermogravimetric analysis (a) and activation energy (*Ea*) (b) of the virgin LDPE film virgin measured at heating rate of 10 °C min^{-1} in N_2. The solid and dashed lines correspond TG and DTG curves, respectively.

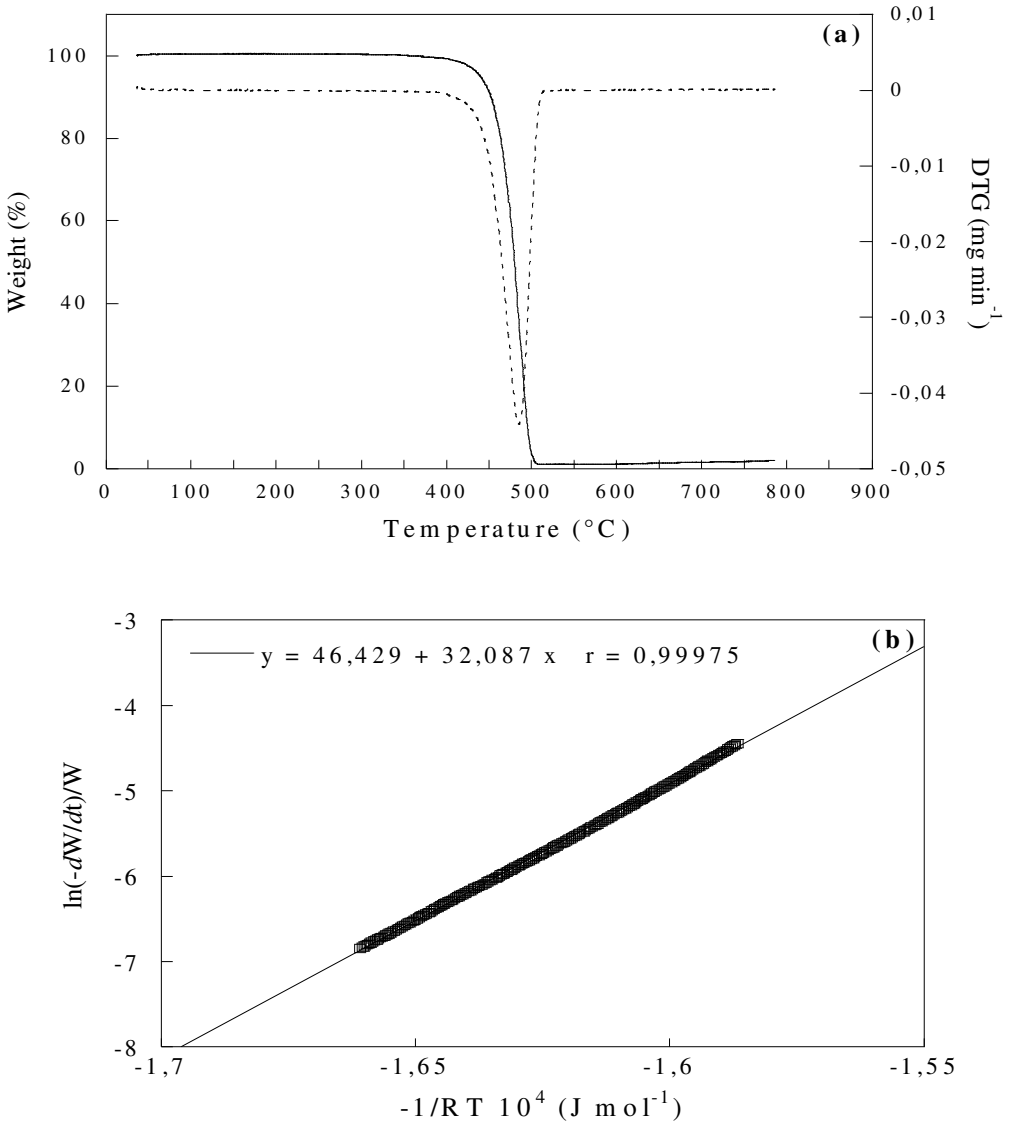

Figure 3. Thermogravimetric analysis (a) and activation energy (*Ea*) (b) of the LDPE film C4-16 m cell measured at heating rate of 10 °C min^{-1} in N_2. The solid and dashed lines correspond TG and DTG curves, respectively.

Table 1. Results obtained for the degradation of virgin LDPE and for the samples collected from the waste site.

Sample	Temperature[a] (°C)	Weight loss[b] (%)	Ea[c] (kJ mol^{-1})	r[c]	Dump age (years)	Depth (m)
LDPE virgin	458.1	98.7	230.63 334.46	0.9983 0.9997	-	-
LDPE C9	490.5	97.9	368.92	0.9998	2-3	8
LDPE C4	488.2	98.7	349.95	0.9999	9-10	11
LDPE C4	485.1	98.9	340.19	0.9997	9-10	12
LDPE C4	485.1	99.1	320.87	0.9997	9-10	16
LDPE C3	490.5	95.5	386.78	0.9995	9-10	9
LDPE C3	485.9	97.5	309.86	0.9992	9-10	10

[a] measure on DTG curve.
[b] measure on TG curve.
[c] determine using a Freeman-Carroll method.

samples of the waste as a function of waste age and depth. For LDPE samples taken from the same cell, the *Ea* decreases with an increase in depth due to the formation of degradation products which causes crystallinity changes, chain scission, and oligomers formation. The results indicated possible changes in the chemical structure during degradation of the material in the landfill, which occurs through several mechanisms. The samples that presented the best results had higher waste ages of up to nine years.

The LDPE are present in high percentages in the waste and they demonstrated an environmental degradation based on changes in the crystallinity after nine years in the landfill site.

ACKNOWLEDGMENTS

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

REFERENCES

Duchin F, Lange G (1998). *Strutural Change and Economic Dynamics* 9, 307- 331.
Grisa AMC, Paese C, Dotto OJ, Nicola R (2012). J. Water Resource and Protection, 04, 16-24.
Haider N, Karlsson S (1999). *Polymer Degradation and Stability* 64, 321-328.
Hatakeyama T, Quinn FX (1994). *Thermal Analysis*, John & Willey Sons, UK.
Kawai F, Watanabe M, Shibata M, Sudate Y (2002). *Polymer Degradation and Stability* 76, 129-135.
Liu NA, Fan WC (1999). *Thermochimica Acta* 338, 85-89.
Poletto M, Zeni M, Zattera AJ (2011). *Journal of Applied Polymer Science* , 33, 123-130.
Viletti MA, Crespo JS, Soldi MS, Pires ATNR, Borsali V. Soldi (2002). J. Thermal Analysis and Calorimetry 67, 295-303.
Zattera AJ, Bianchi O, Oliveira ROV, Canto LB, Ferreira CA, Zeni M (2006). *Progress in Rubber, Plastic and Recycling* , Shrospshire- UK, 22, 168-180.

How to cite this article: Grisa A.M.C., Janaina S.C and Zeni M (2013). Kinetic parameters for degradation of municipal waste polymer. J. Res. Environ. Sci. Toxicol. 2(7):126-130