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Application of the principal component analysis method in the biodegradation polyurethanes evaluation

Juliana Regina Kloss [a], Tiago Hommerding Pedrozo [a], Heveline Dal Magro Follmann [a], Patricio Peralta-Zamora [b], Jair Alves Dionísio [c], Leni Akcelrud [d], Sônia Faria Zawadzki [a,*], Luiz Pereira Ramos [e]

[a] Laboratório de Polímeros Sintéticos, Universidade Federal do Paraná, Curitiba, Brazil
[b] Laboratório de Química Ambiental e de Materiais, Universidade Federal do Paraná, Curitiba, Brazil
[c] Departamento de Solos e Engenharia Agrícola, Universidade Federal do Paraná, Curitiba, Brazil
[d] Laboratório de Polímeros Paulo Scarpa, Universidade Federal do Paraná, Curitiba, Brazil
[e] Laboratório de Química de Fitobiomassa, Universidade Federal do Paraná, Curitiba, Brazil

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ABSTRACT

In the last decades polyurethanes have been studied as biodegradable and biocompatible materials, especially for the use in the biomedical engineering area. In the present work, the biodegradation of polyurethanes of different composition was evaluated by Fourier Transformed Infrared spectroscopy (FTIR) and Principal Components Analysis (PCA). In general, it was noticed that the samples with 1,4-butanediol containing the lowest glucose content constituted a group that was considerably different from all the others. These samples did not show any considerable variations in their infrared spectra within four months of biodegradation and a more significant variation was observed only after 12 months of biodegradation. It was also observed that the polyurethane samples based on sucrose were more biodegraded. The use of the chemometric tools particularly the Principal Component Analysis applied to the infrared spectra allowed us to reach a better identification of the chemical modifications occurred before and after the biodegradation.

1. Introduction

The environmental impact caused by the growing use of materials derived from petroleum, a non-renewable source, is a serious problem to be solved since these materials have a large degradation time. They are getting accumulated and this fact increases the environmental pollution until alarming proportions (especially in countries in both political and economical growth) [1–4]. The interest in use of alternative products based on natural sources for the manufacture of plastic materials has became a political goal in various sectors of the society mainly if this new materials exhibit biodegradable characteristics [4]. Biodegradable polymers research arose in the sixties. Preferentially they have to show durability in usage and degradability after disposal. Besides, they also can be prepared from renewable sources. As consequence, it would be possible to have a better control of the solid residues and smaller quantities of the garbage disposed in the sanitary land fills or sent to the incinerators. The main barrier to biodegradable packaging is the manufacturing cost when compared to the traditional polymers [5–7].

In the last years, polyurethanes (PUs) have been studied as biodegradable and biocompatible materials especially for the use in the biomedical engineering area [8–10]. When biodegradability is required it is important that the material have chemical groups in the molecular chain that allow accessibility of the enzymatic system. Therefore, an effective biodegradation process is associated to the suitable polyurethane compositions [11,12].

The infrared spectroscopy can be used to corroborate the biodegradation of polymeric materials, mainly by monitoring the variation of characteristic bands. In general the structural changes are minima and a reliable interpretation depends on a right analysis of a set of spectral data. The application of this technique usually represents a hard and extensive work, which can induce to erroneous interpretations or losses of relevant information. In general, the interpretation of spectral data can be significantly favored by the use of multivariate tools, markedly by Principal Component Analysis (PCA). The use of this method in FTIR spectra, allows a better identification of the spectral differences among the samples. Only by applying chemometric tools it is possible to identify the minima differences between all the samples spectra. The PCA method also enables to segregate the samples in determined groups, it getting easier the data interpretation.

The PCA method can be considered as a special tool whose data are integrally used without any loss of information. The PCA application represents a gain to a perfect experimental data acquisition.

PCA is mathematically defined as an orthogonal linear transformation system that changes the data to a new coordinate system such

* Corresponding author.
E-mail addresses: juliana.kloss@gmail.com (J.R. Kloss), thip@bol.com.br (T.H. Pedrozo), heveline_follmann@yahoo.com.br (H. Dal Magro Follmann), zamora@quimica.ufpr.br (P. Peralta-Zamora), zawadzki@quimica.ufpr.br (S.F. Zawadzki).

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that the greatest variance by any projection of the data comes to lie on the first coordinate (called the first principal component), the second greatest variance on the second coordinate, and so on.

The "scores" graph which represents the position of the sample plots in the reduced-dimensional space provides a window statistically privileged to the observation of the points in the *n*-dimensional space [13–15].

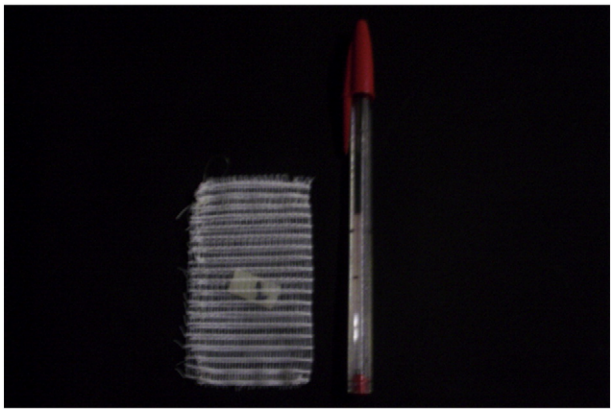

Fig. 1. Preparation of the PU Samples to the biodegradation assay: 1 piece of each sample in small packages.

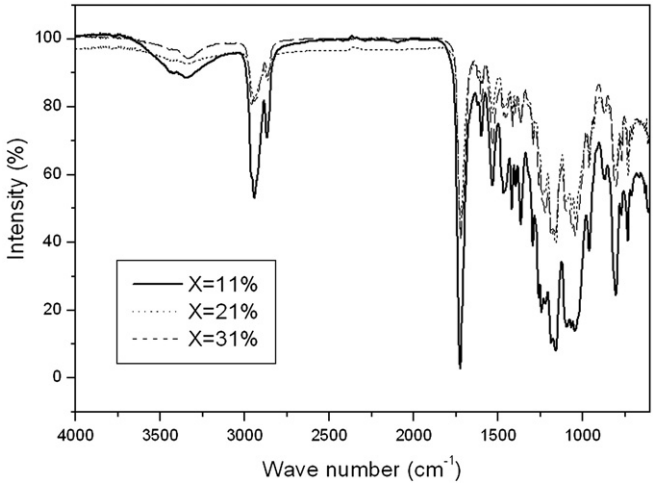

Fig. 2. Typical FTIR spectra of the pure PU samples before biodegradation (Hard segment content (X) 11 or 21 or 31%).

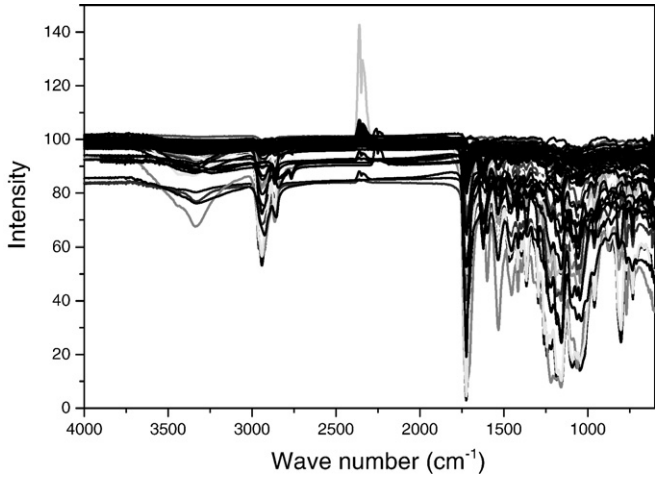

Fig. 3. Infrared spectra of the polyurethanes.

Table 1
Polyurethane samples identification (related to Fig. 4)

Polyurethanes	Sample number (related to Fig. 4)
PU (BDO X=11%)	1,2,3,4,5,6,7
PU (BDO X=21%)	8–14
PU (BDO X=31%)	15–21
PU (GLU X=11%)	22–28
PU (GLU X=21%)	29–35
PU (GLU X=31%)	36–42
PU (SUC X=11%)	43–49
PU (SUC X=21%)	50–56
PU (SUC X=31%)	57–63

The present work shows the different polyurethanes analysis by Fourier Transformed Infrared spectroscopy including the separation of polyurethanes based on different compositions. It was also studied the biodegradation of the different polyurethane samples in the soil: the structural characterization was done through significant chemical changes from the Fourier Transformed Infrared (FTIR) data using multivariated calibration associated to the PCA (Principal Component Analysis) method. In general, the PCA allows the decrease in the dimension of the original data without compromising them. This multivariated analysis took place in the Matlab v.6.5® environment, making use of the PLS-toolbox 1.5 software. The signs were pre-processed through a checking routine of multiplied signs (MSC), in order to increase the rationale signal and to correct the base line [16,17].

2. Experimental

Segmented polyurethanes were synthesized in bulk by a two-step procedure. In the first step, a terminated diisocyanate prepolymer was prepared from hydroxyl terminated poly(ε-caprolactone) dried before reaction (80 °C; 10 mmHg; 12 h) and toluene diisocyanate (TDI) ([NCO]/[OH]=1,1). In the second step, the prepolymer was chain extended by an equimolar amount of 1,4-butanediol (BDO), or crosslinked with two different agents, sucrose (SUC) or glucose (GLU) [16–18].

The PU samples were obtained by casting films without any solvent: PU, as a viscous liquid, was poured to round moulds (diameter: 20 mm and thickness: 3 mm) and/or to square moulds (100×100 mm×3 mm), which were put in a vacuum oven (100 °C; 600 mmHg; 48 h); for the thermal cure.

The PCL portion was called soft segment (SS) and TDI/BDO or TDI/GLU or TDI/SUC resultant links were called hard segments (HS). The polyurethanes had 3 different hard segment contents (X): 11, 21 and 31% for each series (BDO or GLU or SUC) [16,17]. The PU samples (10 mm×20 mm×3 mm) were previously weighted and they were put in small closed screen packages (Fig. 1).

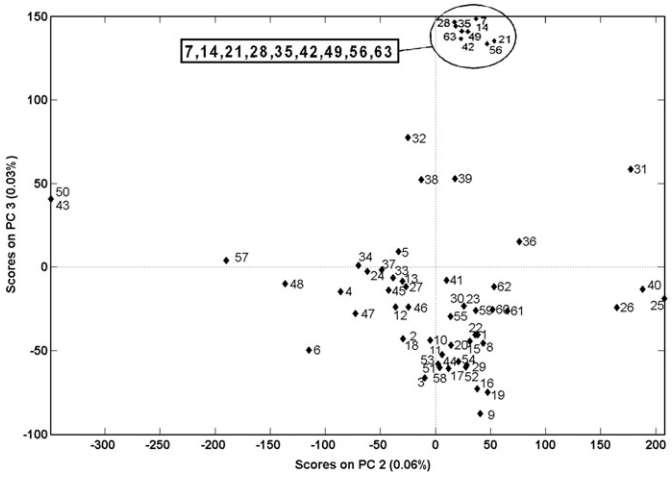

Fig. 4. Scores graphic—all polyurethanes samples.