EVALUATION OF LEATHER BIODEGRADABILITY

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This paper presents a study regarding the biodegradability of tree types of finished leathers tanned with different tanning agents: based on Chromium (III), based on Ti-Al, based on Ti-Zr. For assessment of leather biodegradation, EN ISO 20200:2005 was used as method. Physical-chemical analyses were performed on leathers at initial state, after 90, 120 and 220 days of composting. The conclusion of the study is that all types of tanned leather studied undergo the biodegradation process but at different rates. A hierarchy was established for leathers taken in this study, as follows: leather tanned with Ti-Al, leather tanned with Ti-Zr, leather tanned with chromium, where chromium (III) tanned leather has the lowest rate of biodegradability.

Keywords: leather tanned with inorganic salts, composting, biodegradation.

INTRODUCTION

Sustainable disposal of chromium tanned leather wastes is essential under current legislation and thus an appreciation of the extent of leather decomposition is essential.

The microbial decomposition of tanned leathers is poorly understood with relatively few reported studies existing. Leather, containing high levels of nitrogen (ca. 16%) is generally considered a high quality resource capable of degrading readily. However, the tanning process, whereby tanning agents are incorporated into the collagen matrix, results in the reduction of substrate quality and reduced microbial decomposition.

Relatively little is known about the toxicity of Cr(III) towards microorganisms. Generally, heavy metal toxicity affects bacterial growth, morphology, and biochemistry (Aftab, 2006; Bhat *et al.*, 1998; Pillai and Archana, 2012) and is usually via one of three mechanisms: (1) blocking of essential functional groups, (2) displacement of essential ions, (3) modification of active conformation of biological molecules.

In the past years, few determinations of leather biodegradability have been made using compost similar to the one used for plastics and which accelerate the natural degradation process (Thanikaivelan *et al.*, 2004; Pantazi *et al.*, 2014) or under natural conditions (Bacardit *et al.*, 2011; Chirila *et al.*, 2014).

In this study, investigations into the microbial decomposition of leather, under a variety of simulated environmental conditions, were performed in accordance with standard EN ISO 20200:2005 - Plastics - Determination of the degree of disintegration of plastic materials under simulated composting conditions in a laboratory-scale test. The method determines the degree of leather disintegration at laboratory scale under conditions simulating an intensive aerobic composting process.

The paper presents a comparative study regarding biodegradation in composting environment of various leathers, such as chrome, Ti-Al and Ti-Zr tanned leathers. Modification of some leather characteristics was monitored for 220 days and differences are discussed.

EXPERIMENTAL

Materials

Finished bovine leathers tanned with different tanning agents: finished bovine leathers tanned with tanning agents based on titanium and zirconium (P_{Ti-Zr}), (Crudu *et al.*, 2012; Adiguzel Zengin *et al.*, 2012; Mutlu *et al.*, 2014), finished bovine leathers tanned with tanning agents based on titanium and aluminum (P_{Ti-Al}), (Crudu *et al.*, 2014; Deselnicu *et al.*, 2014, Mutlu *et al.*, 2014), finished bovine leathers tanned with tanning agents based on chromium (III) (P_{Cr}). The chemicals used in the operations were those normally used in the leather industry.

Methods

For assessment of leather biodegradability Standard EN ISO 20200:2005 - Plastics - Determination of the degree of disintegration of plastic materials was used under simulated composting conditions in a laboratory-scale test.

For compost, the following parameters have been considered: temperature: 15-60°C; humidity: 50-60%; oxygen: 15-20%; C/N: 20-30/1.

Four leather samples of each type of tanned leathers were placed in the boxes with compost and one piece of each type of leather was analyzed after 60, 90 and 220 days for the characteristics mentioned below.

For determination of physical-chemical characteristics of leather the following standards were used:

- SR EN ISO 3380:2003 - Leather - physical and mechanical tests - determination of shrinkage temperature up to 100 degrees C;
- SR EN ISO 4045:2008 - Leather - chemical tests - determination of pH.
- SR EN ISO 4684:2006 - Leather - chemical tests - determination of volatile matter;
- SR EN-ISO 4048:2008 - Leather - Chemical tests - Determination of matter soluble in dichloromethane and free fatty acid content;
- SR EN ISO 4047:2002 - Leather - determination of sulphated total ash and sulphated water-insoluble ash;
- SR ISO 5397:1997 - Leather - determination of nitrogen content and "hide substance" - titrimetric method.

The chemicals used for analytical tests were of laboratory grade.

RESULTS AND DISCUSSION

Composition of animal skin consists in: water ca. 65%, proteins ca. 33%, mineral matter ca. 0.5%, fatty substances 2-6% (cattle, calf). Proteins are formed by globular proteins ca. 3.5% and fibrous proteins from which collagen represents ca. 98%. During leather manufacture the collagen interacts with organic and inorganic substances which combine chemically with collagen or are physically deposited within the interfibrillar spaces. The main components of the tanned leather are: "hide substance", fatty matter, humidity, water-soluble organic substances, water-insoluble organic substances, ash. Those components which are likely to be degraded have been analyzed in this study: volatile matter, matter soluble in dichloromethane, sulphated total ash, shrinkage temperature, nitrogen content and pH. All these physical-chemical analyses were performed on leather samples in the initial state, after 90, 120 and 220 days of composting process. Figures 1-5 present the evolution of these components over time.

Measurement of the Shrinkage Temperature

Shrinkage temperature of tanned leather is an indicator of the stability of collagen. It was measured to determine the degree of deterioration in collagen. The shrinkage temperature decreases over time for all type of leathers (Figure 1). Decreasing rate was 12% for chrome tanned leather (P_{Cr}), 17% for Ti-Zr tanned leather ($P_{Ti\text{-}Zr}$) and 18% for Ti-Al tanned leather ($P_{Ti\text{-}Al}$). A detanning process is initiated during biodegradation.

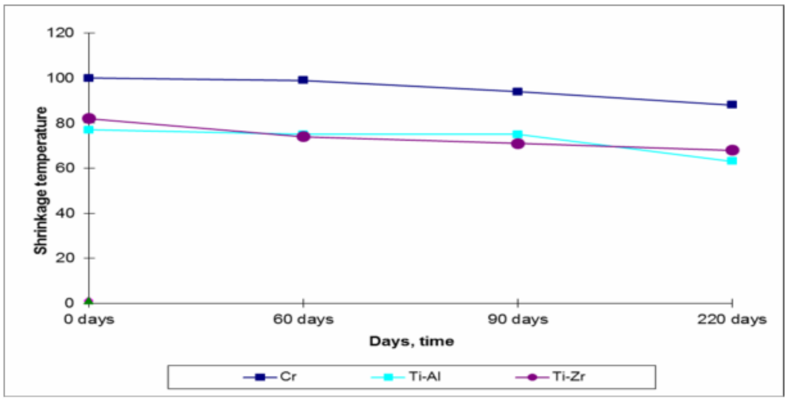

Figure 1. Modification of shrinkage temperature

Determination of pH

pH was determined in water extract and increased over time for all type of leathers during biodegradation process (Figure 2). There is a relation between the pH value and shrinkage temperature. It can be said that loss of stability of the collagen molecule can occur as a result of hydrolytic degradation which occurs when tanned leather is held under warm moist conditions at acidic pH level (Haines, 1987). This type of chemical degradation leads to a progressive loss of strength and a fall in shrinkage temperature.

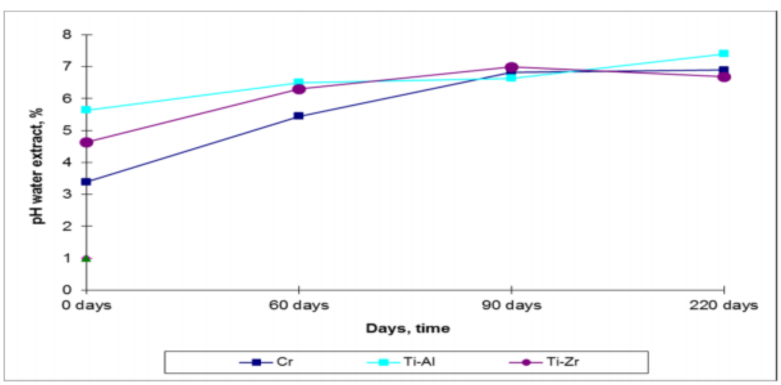

Figure 2. Modification of pH

Determination of Volatile Matter

Volatile matter consists mainly in humidity, but also other volatile matter appears as a result of reaction of peroxide radicals with organic constitutes of leather, and dyes, tanning agents and fatliquors, breaking bonds between the said products and collagen. For the first 90 days evolution of volatile matter is comparable for all types of leather; after 220 days degradation processes intensified and volatile matters content increased by 273.7% for Ti-Al tanned leather (P_{Ti-Al}), by 122.63% for Ti-Zr tanned leather (P_{Ti-Zr}) and by 7.96% for chrome tanned leather (P_{Cr}) (Figure 3).

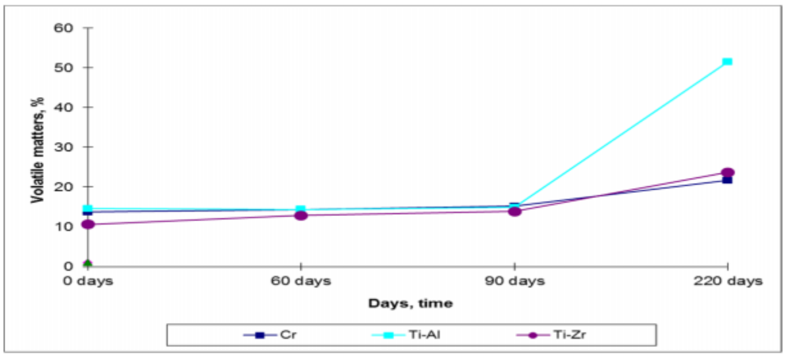

Figure 3. Modification of volatile matters

Determination of Matter Soluble in Dichloromethane

The content of matter soluble in dichloromethane decreased by 60-90% for all types of leather after 60 days of composting, due to biodegradation process and breaking of chemical bonds of fatliquors to collagen (Figure 4):

a) after 90 days matter soluble in dichloromethane decreased by 59.2% for Ti-Al tanned leather (P_{Ti-Al}), by 68.87% for Ti-Zr tanned leather (P_{Ti-Zr}) and by 94.60% for chrome tanned leather (P_{Cr});

b) after 220 days matter soluble in dichloromethane decreased by 80.69% for Ti-Al tanned leather (P_{Ti-Al}), by 99.95% for Ti-Zr tanned leather (P_{Ti-Zr}) and by 99.51% for chrome tanned leather (P_{Cr}).

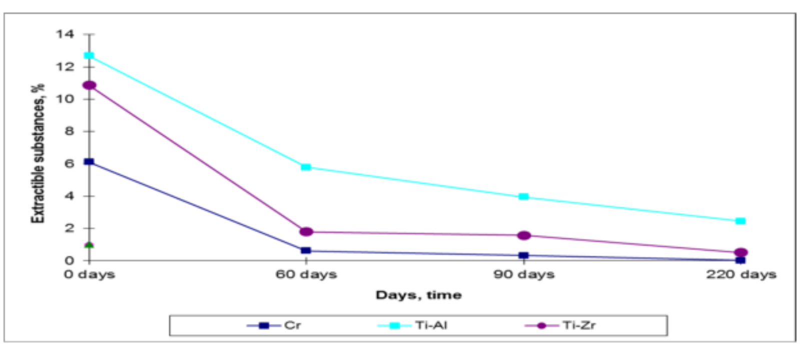

Figure 4. Modification of matter soluble in dichloromethane

Determination of Total Ash

Total ash consists of inorganic salts and tanning agents oxides from leather. Total ash content (Figure 5) increased over time for all types of leather due to the mineralization processes produced during composting:

a) after 90 days total ash increases by 59.2% for Ti-Al tanned leather (P_{Ti-Al}), by 64.93% for Ti-Zr tanned leather (P_{Ti-Zr}) and by 26.47% for chrome tanned leather (P_{Cr});

b) after 220 days total ash increases by 162.69% for Ti-Al tanned leather (P_{Ti-Al}), by 82.59% for Ti-Zr tanned leather (P_{Ti-Zr}) and by 53.48% for chrome tanned leather (P_{Cr}).

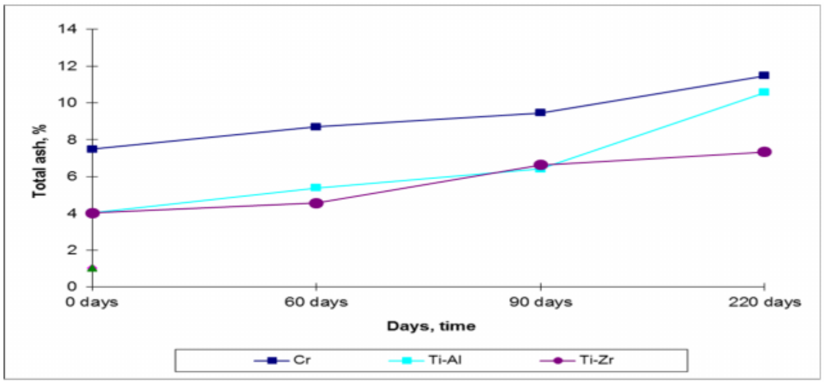

Figure 5. Modification of total ash

Determination of Kjeldahl Nitrogen

Nitrogen content of leather (Figure 4) decreases slowly for the first 90 days of composting; after that, after 220 days, an important reduction is observed due to the biodegradation process.

a) after 90 days nitrogen content decreases by 18.22% for Ti-Al tanned leather (P_{Ti-Al}), by 26.56% for Ti-Zr tanned leather (P_{Ti-Zr}) and by 0.3% for chrome tanned leather (P_{Cr});

b) after 220 days nitrogen content decreases by 5.82% for Ti-Al tanned leather ($_{Ti-Al}$), by 35.05% for Ti-Zr tanned leather (P_{Ti-Zr}) and by 3.07% for chrome tanned leather (P_{Cr}).

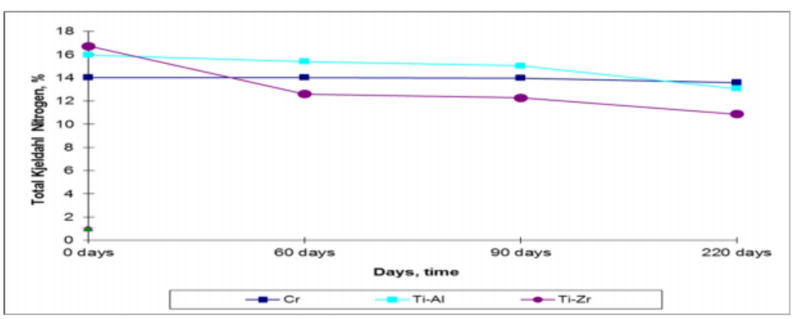

Figure 4. Modification of Kjieldal nitrogen

CONCLUSIONS

The paper presents a comparative study regarding biodegradation of various leathers, such as chrome, Ti-Al and Ti-Zr tanned leathers in composting environment, in accordance with Standard EN ISO 20200:2005 - Plastics - Determination of the degree of disintegration of plastic materials under simulated composting conditions in a laboratory-scale test. Composting causes a physical degradation on leathers, a chemical degradation with dehydration, a partial scission of protein chain of the collagen, detanning and loss in oils due to volatilization and/or decomposition.

A significant evolution of the properties of the leather tanned can be observed after 60 days of composting. All types of tanned leather studied undergo biodegradation processes, but at different rates. Leather tanned with Ti-Al showed a higher rate of biodegradation than leather tanned with Ti-Zr and chrome tanned leather.

Acknowledgements

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