DECORATIVE EPOXY COMPOSITES WITH INORGANIC FILLERS WITH THE ADDITION OF ASH RICH IN CR$_2$O$_3$ FROM WASTE HIDE PROCESSING

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The objective is to embed epoxy polymer waste from hides with basic chromium salts in a matrix in order to prevent its toxic action in the presence of environmental factors. Leather fragments resulting from different operations are chrome leather waste and may sum up to 25% of skin subjected to processing. The waste was thermal treated at 800, 900 and 1000°C - 3h, in order to obtain ash with CR$_2$O$_3$. 17 recipes with 60% resin and 40% fillers (Urcani quartz, chemically treated talc, yellow silica granules) pigmented with CR$_2$O$_3$ ash (0.1-0.6%, 1%) were developed.

Materials used are cheap and easy to find. Decorative polymer composites with recycling inorganic residues with a content of chromium (obtained by calcinations bovine tanned hide waste with basic chromium salts) are obtained using 3 technological homogenizations. X-ray, X-ray fluorescence, optical microscopy and color analysis were performed.

Keywords: epoxy polymer, CR$_2$O$_3$ ash, decorative composites.

INTRODUCTION

Epoxy resin is an organic macromolecular compound that becomes an inert compact mass during a chemical reaction.

Chemical reaction for hardness can be started by:
• Addition of hardener;
• Heat treatment.

Studies have focused on recovery of residual chromium use in biological processes with microorganisms, algae, fungi and vermiculite [2], membrane processes and nano filtration complexion - ultra filtration, ion exchange processes [4], adsorption on various natural and synthetic materials (diatomite, bentonites, bauxite, alumina, activated carbon from various sources, geo-polymer, poly aniline), electro coagulation, electrochemical recovery.

Attempts to recover chromium from tannery waste products were the subject of a patent, “Recovery of potential energy values and chromium from tannery leather wastes” by H. A. Muralidhara, Fairfax, Va. June 1, 1982.


Studies for chromium waste recovery were directed towards chromium pigments, ceramic materials, including refractory ceramics, inclusion of residual chromium in cement. For chromium in tannery waste, to explore the possibility of reintroducing the tanning process but also to trap in a complex mineral waste [5], with the possibility of using the compound in the production of ceramic glazes and glass and the composition of construction materials: concrete, bricks, ornaments.
MATERIALS AND EQUIPMENT

Materials used for experiments [1]

- epoxy resin - a mixture of Biphenyl A and Biphenyl F, 1:1;
- hardener - Ancamine 2686, 2:1 ratio;
- talc;
- Uricani Quartz;
- yellow granular silica;
- ash from leather with chrome content.

Equipment used

- optical stereomicroscope Leica S4E – LEICA;
- ultrasound shaker S 15h Elmasonic – ELMA;
- X-Ray Diffractometer XRD6000 – SHIMADZU;
- Micro-XRF Spectrometer - ARTAX 400;
- LabScan ® XE color analyzer - HUNTER LAB;
- Hardness meter Durotech – Durometers.

EXPERIMENTAL PART

A total of 43 composition recipes were made by mixing different proportions of raw materials in order to observe the effect of changes in the amount of pigment and filler used.

Samples were performed in polyethylene containers with round shape. The main reaction for obtaining the composite is illustrated in Figure 1.

![Figure 1. Chemical reaction of resin (the mixture) and the hardener](image)

RESULTS AND DISCUSSION

Analyses have been carried out both on raw materials and composite products obtained. In this way more detailed information about materials and products could be obtained.
Optical microscopy [1] could offer information on the degree of fineness of raw materials - Figure 2 - and about the samples made - Figure 3.

![Figure 2. Filer fineness (a, b), pigment (c)](image)

Figure 2. Filer fineness (a, b), pigment (c)

X-ray diffraction analysis for used ash - Figure 4, was made by a comparison of their spectra with diffraction spectra for $\text{Cr}_2\text{O}_3$, $\text{Na}_4(\text{CrO}_4)(\text{SO}_4)_3$, $\text{CaCrO}_4$. We observe large amounts of $\text{Cr}_2\text{O}_3$ and $\text{Na}_4(\text{CrO}_4)(\text{SO}_4)_3$, because in the process of skin processing and tanning $\text{NaCl}$, $\text{CaO}$, $\text{Cr(OH)SO}_4$ are mainly used.

![Figure 4. X-ray spectrum of ash](image)

Figure 4. X-ray spectrum of ash

X-ray fluorescence analysis provides information regarding element identification. The detected elements were Cr - in large amount, Ca - coming from processing with $\text{CaOH}$ but also heavier elements, Bi, Fe, Cu, most likely impurities. Figure 5 shows the identification of elements present in the ash obtained by burning the tanned leather, with chromium salts.
Table 1 contains the elements and obtained values.

<table>
<thead>
<tr>
<th>Identified element</th>
<th>Reference Cr₂O₃ Peak intensity</th>
<th>Ash at 800°C Peak intensity</th>
<th>Ash at 900°C Peak intensity</th>
<th>Ash at 1000°C Peak intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>529</td>
<td>7032</td>
<td>3692</td>
<td>10832</td>
</tr>
<tr>
<td>Cr</td>
<td>1732521</td>
<td>825810</td>
<td>1626459</td>
<td>1308442</td>
</tr>
<tr>
<td>Bi</td>
<td>3578</td>
<td>1475</td>
<td>3440</td>
<td>2455</td>
</tr>
<tr>
<td>Fe</td>
<td>-</td>
<td>3279</td>
<td>6490</td>
<td>5224</td>
</tr>
<tr>
<td>Cu</td>
<td>-</td>
<td>-</td>
<td>2195</td>
<td>-</td>
</tr>
</tbody>
</table>

Hardness of obtained samples was determined using a hardness meter - °Shore. Hardness measurement method is by indentation – Table 2.

Shore hardness is a method commonly used to characterize “soft” products – rubber, plastics, elastomers, polyolefin, fluoro-polymer, vinyl.
A Shore scale - produced “softer” rubber type.
D Shore scale - produced “heavier” type (over 95°Shore).

<table>
<thead>
<tr>
<th>Epoxy composite</th>
<th>Sample content</th>
<th>Hardness test °ShA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resine60%+quart 40%</td>
<td>Reference</td>
<td>95</td>
</tr>
<tr>
<td></td>
<td>0.1% ash</td>
<td>94</td>
</tr>
<tr>
<td></td>
<td>0.2% ash</td>
<td>96</td>
</tr>
<tr>
<td></td>
<td>0.3% ash</td>
<td>94</td>
</tr>
<tr>
<td></td>
<td>0.4% ash</td>
<td>95</td>
</tr>
<tr>
<td></td>
<td>0.5% ash</td>
<td>96</td>
</tr>
<tr>
<td></td>
<td>0.6% ash</td>
<td>96</td>
</tr>
<tr>
<td></td>
<td>1% ash</td>
<td>93</td>
</tr>
</tbody>
</table>
Colorimetric analysis [1] - Figure 6 - provides visible reflectance spectra (400-700 nm) of those four powders, after which the next assumptions have been issued:

1. Identical form of spectra and the same wavelength for reflectance - 540 nm (green) reveals the same substance in all four samples.
2. Differences in height and width versus the blank sample test illustrates a less content in the predominant substance Cr₂O₃ and the presence of other substances that reflect both towards smaller wavelength (blue) and higher (red).
3. Reflection spectrum for samples made at high temperatures is approaching from reference reflectance spectrum.

![Figure 6. The reflection spectra of analyzed samples](image)

![Figure 7. Visible wavelengths](image)

In terms of samples brightness, we can observe a steady growth - Figure 8, the lower value is for reference sample. This shows the presence of light colored substances and calcium identifying in X-ray fluorescence analysis, confirms the presence of calcium oxide (white).

![Figure 8. Brightness chrome ash](image)
CONCLUSION

The overall objective of this paper was inertization of waste hides tanned with chromium salts to prevent potentially toxic environmental action in case of improper storage (subject to external factors: temperature, humidity, interaction with some chemicals present in soil or air).

43 recipes were developed for obtaining decorative composite inorganic polymer valuing the residues containing chromium, using three types of technological homogenization.

They used cheap materials and nondeficit.

A simple technological process was developed without requiring special conditions (sophisticated equipment, high temperatures and pressures) and it is practically working at room temperature in open containers of polypropylene with intermittent mixture mechanical and ultrasonic type.

The composite decorative items resulting that have been characterized using modern methods of investigation:

- Optical microscopy;
- Spectrochromatography;
- Determination of hardness using hardness meter Durotech (°Share);
- X-ray diffraction.

After interpreting the results, 22 types of decorative composite product were selected (which have the best homogeneity / pore size, uniform color).

Positive results obtained from laboratory experiments lead us to conclude further research to pilot level – semi-industrial, in order to achieve practical application products, such as:

- Insulator (phase porous);
- Compact floor area of traffic;
- Cast and / or processed by different technologies;
- Other applications in various fields (art, aviation, consumer goods).

REFERENCES


