

# Preparation and Characterization of Polyamide-Leather Wastes Polymer Composites

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**ABSTRACT:** Chrome tanning of leather improves its appearance, but at the same time, it emits both solid and liquid wastes. These solid wastes mainly after shaving process present in large amount causing hazard to the environment. Leather wastes were disintegrated to prepare hide powder and mixed with polyamide (nylon 6) in different ratios. The physical, mechanical and thermal properties of different composites were investigated, which showed enhancement in physical characters but

decreasing in mechanical properties. The charred residue increases by increasing the presence of leather waste filler. Morphological studies were performed on the fractured surface of composites showed uniform and fine particles dispersion. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 446–451, 2010

**Key words:** nanocomposite; polyamide; thermogravimetric; analysis waste; X-ray

## INTRODUCTION

Chrome leather wastes, leather scraps, or chrome shavings are produced in post-tanning operations such as trimming, splitting, and shaving. Processing of one ton wet salted hide yields only 200 Kgs of leather and produce over 600 Kgs as a rejected wastes.<sup>1</sup>

These large quantities of solid leather wastes are disposed in landfill. Environmental restrictions and escalating landfill have encouraged leather industry to develop cleaner technology by minimizing wastes generated and maximizing their recycling.<sup>2</sup> In past decades, leather researchers have made a lot of efforts to study the reuse of leather wastes.

Before 1970 reports dominantly focused on uses not requiring extensive pretreatment of tanned wastes, including the manufacture insulators, building materials, fibrous sheets, and shoe soles.<sup>3</sup> Between 1970 and 1993, a lot of publications and patents concerning leather wastes hydrolysis to recycle amino acids and peptides for use in feeds and fertilizers.<sup>4–8</sup>

Wet air oxidation and incineration of leather wastes processing were used to recycle chrome shaving.<sup>9</sup> Researchers studied the effectiveness of leather waste as filler or as a processing aid rubber formulation, to improve vulcanization character, me-

chanical properties,<sup>10</sup> and as filler of butadiene-acrylonitrile rubber.<sup>11</sup>

Nylons are one of the most widely used engineering thermoplastics such as in automobile parts, electrical, electronic, packaging, textiles and consumer applications because of their excellent mechanical properties.<sup>12–14</sup>

However, limitations in mechanical properties, the low heat distortion instability of pure nylons and its expensive price have prevented their applications to structural components. Hence numerous efforts have been undertaken to use nylons as a matrix for composite by adding inorganic fillers such as glass beads,<sup>15</sup> Kaolin,<sup>16</sup> aluminatrichydrate, clays, silica,<sup>17</sup> flyash,<sup>18</sup> wollastonite,<sup>19</sup> mica,<sup>20</sup> and calcium carbonate.<sup>21</sup>

In this investigation leather wastes were blended with nylon 6 polymer, to satisfy the environmental needs, reduce cost of polymer production, and finally to improve the properties of polymer. The influence of this addition as a filler on mechanical, physical and thermal stability properties were investigated.

## MATERIALS AND METHODS

### Materials

- Leather wastes were supplied from tannery from misr alkadima region, Egypt. These wastes were subjected to multistages disintegration to prepare powder.
- Nylon 6: was a product from tairilag, Taiwan.

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**TABLE I**  
Physical Analysis of Leather Wastes

pH	3.8
Moisture %	14
Mineral ash %	8.23
Ash content %	12.3

## Methods

Preparation of nylon 6/leather wastes composites

Nylon 6 based composites were prepared by mixing the components in a Brabender apparatus operating at 230°C and 70 rpm for 5 min. The mixing ratios of Nylon 6/leather wastes were 98 : 2, 96 : 4, 92 : 8, and 88 : 12 in addition to blank sample. Nylon 6 and Nylon 6 based leather wastes composites were compressed to sheets form between two stainless plates pressed at 160°C for 5 mins at 100 bar was for 5 min, then the plates were rapidly cooled to room temperature.

FTIR analysis

IR spectra of leather wastes were carried out using Nexus 670 FTIR spectrophotometer, Nicolet, USA, over range 400–4000  $\text{cm}^{-1}$  with resolution 4  $\text{cm}^{-1}$ .

Organic analysis

The analysis was carried out on vario ELELementar instrument.

X-ray fluorescence analysis

The X-ray analysis was carried out using Axios, WD-XRF sequential spectrometer (Panalytical, 2005).

Mechanical testing

Dumbbell shape specimens with standard dimensional (5 × 1 and 4 mm neck width) were used for the measurements of tensile strength ( $\sigma$ ) and strain ( $\epsilon$ ) at yield and at rupture. The tests were carried out by Zwick Machin (Model 1425) according to (ASTM 684).

Hardness

Hardness tests were carried out using the AMSLER OTTO WOLPPERT-WERKE GMBH Apparatus D 6700 at 36.5 Kp.

Water absorption (Swelling character)

Samples were weighed before water treatment and then immersed in water for different times. After re-

moval they were webbed with tissue paper to remove excess water on the surface then reweighed, the process was repeated after regular time intervals to find out the amount of water absorbed as a function of time.

Water absorption capacity ( $\omega$ ) was determined from the relationship.<sup>22</sup>

$$(\omega) = \frac{W - W_0}{W} \times 100 = \dots\%$$

Where  $W_0$  and  $W$  are the weights before and after immersion in water respectively.

Scanning electron microscope

Samples (1  $\text{cm}^2$ ) were subjected to sputter coating of gold ions which act as conducting medium during scanning with Jeol scanning microscope type JXA-840A, Japan.

Thermogravimetric analysis

The thermal properties were determined using TGA Perkin Elmer, with rate 10°C/min, temperature range from room temperature up to 500°C.

## RESULTS AND DISCUSSION

### Characterization of leather wastes used

Leather wastes were characterized through different methods of analysis and the obtained data were represented in the following tables:

Physical properties of sample

The properties of leather wastes are shown in Table I.

Organic constituents

The presence of large amounts of C, H, N may be due to the presence of amino acids, where they are the main constituents of leather waste, they represent about 50% of leather waste (Table II).

**TABLE II**  
Chemical Composition of Leather Wastes

Element	Amount %
C	32.277
H	4.862
N	10.893
S	2.140

TABLE III  
X-Ray Fluorescence Results

Element	Conc. (%)
Na	0.245
Si	0.089
P	0.007
S	0.842
K	0.029
Ca	0.649
Cr	3.560
Cu	0.006
Fe	0.057
Ni	0.013
Zn	0.004
Zr	0.001
Cl	2.667
Ti	0.006
Sr	0.007
Al	0.026
Mg	0.013
Ba	0.017
Lowest organic ignition	91.76
Total	99.998

X-ray fluorescence analysis (XRF)

X-ray fluorescence spectrometric studies were carried out to determine the elemental constituents in leather wastes. The obtained results are shown in Table III, from the table it is clear that Cr represents the highest amounts in the leather wastes followed by Cl, S, and Ca 2.6, 0.842, 0.649, respectively. All elements have few contributions with minor percentage.

FTIR studies

FTIR of leather waste studies were carried out and the results are shown in Figure 1. A broad band can be seen between 3300–3500  $\text{cm}^{-1}$  corresponding to the presence of  $-\text{OH}$  and  $-\text{NH}$  stretching of amino acid in leather wastes, band at 1650 corresponding to  $\text{C}=\text{O}$  of amide group, band at 1540 corresponding to  $\text{NH}$  bending of amino acids, and weak bands in region 1000–1250 resulting from  $-\text{CN}$  and  $-\text{CO}$  groups of leather amino acids.

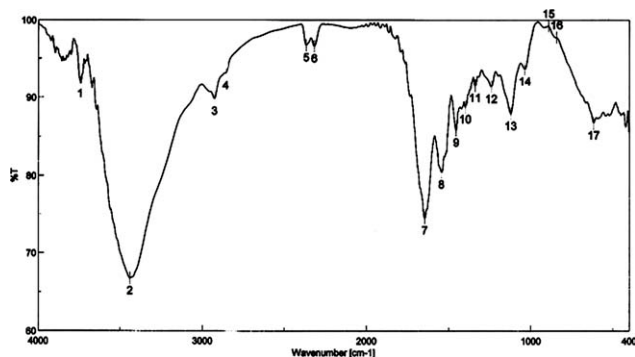


Figure 1 FTIR of leather wastes.

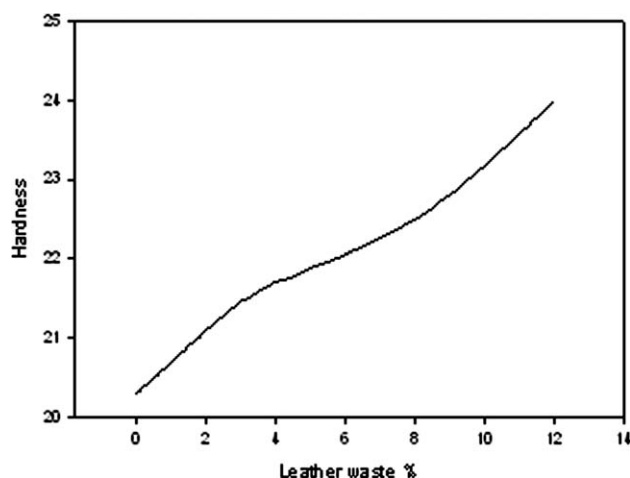


Figure 2 Relation between percentage of leather wastes in the polymer composite and the hardness of samples.

### Properties of nylon 6-leather wastes composites

The mechanical properties of the prepared polymer-waste leather composites were measured and the results are shown in the following sections.

Hardness

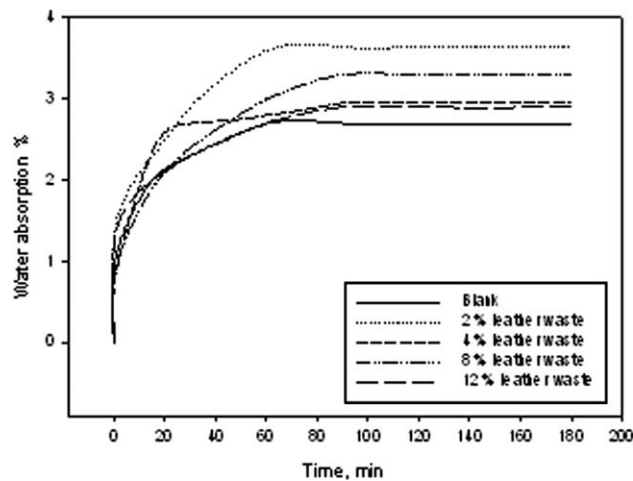
Hardness test is based on the penetration of indenter forced into composite materials. The hardness indentation is inversely related to the penetration values and it is dependent on the elastic modulus and viscoelastic behavior of the material. The obtained results for hardness measurements are plotted in Figure 2. From the figure it can be detected that by increasing leather waste ratios in the composites the hardness of samples increased, which may be due to the presence of solid leather waste powders, that reinforced the prepared polymer composites.

Mechanical results analysis

The mechanical properties of the prepared polymer composites were determined and the obtained results are presented in Table IV.

TABLE IV  
The Mechanical Properties of the Prepared Polymer-Waste Leather Composites

Leather waste %	Tensile strength at yield $\sigma_B$ (MPa)	Tensile strength at Rupture $\sigma_R$ (MPa)	Elongation at yield $\epsilon_B$ %	Elongation at rupture $\epsilon_R$ %
0	49.3	48.33	23.4	24.6
2	48.2	47.5	21.2	22.6
4	44.7	44.8	18	19.3
8	43	42.8	14	15.4
12	41.5	41.2	12	13.6

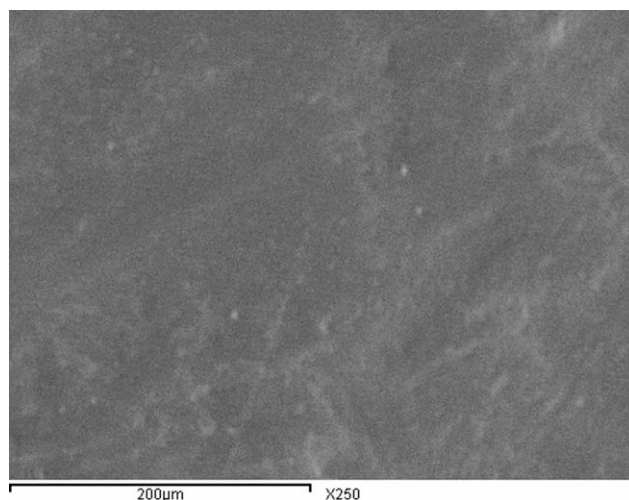


**Figure 3** Water absorption of different ratios between poly amide nylon-6 and leather waste composite.

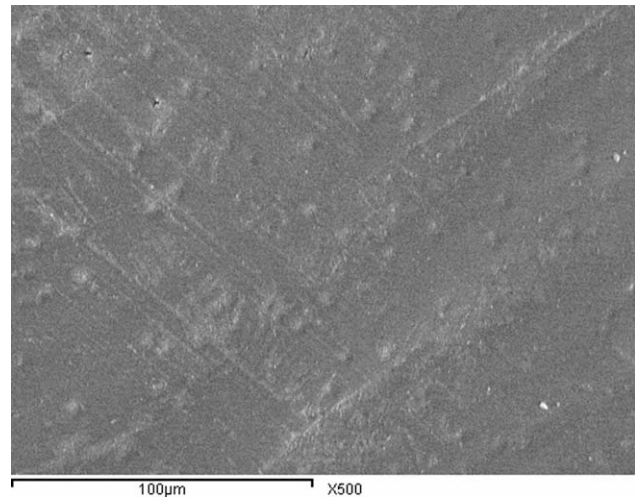
From this table it is clear that, by increasing leather waste in the polymer composites, the tensile strength and elongation % decreased. This reduction in tensile strength and elongation% can be attributed to the weak physical interaction between leather wastes and polyamide (nylon 6) causing reduction in the mobility of the polymer chains, so the composite tends to form a weak structure. By increasing the amounts of wastes the distance between filler particles reduced, so insufficient matrix available for contributing the elongation %.

It can be concluded that, there was no real adhesion between leather filler and the polymer matrix, while the matrix has shrunk down around the filler powders by differential thermal contraction.

These results agree with literature,<sup>23</sup> which showed that incorporation of leather wastes into PVC caused an increase in density and hardness, whereas tensile properties and elongation were decreased.



**Figure 4** SEM photograph for blank with.

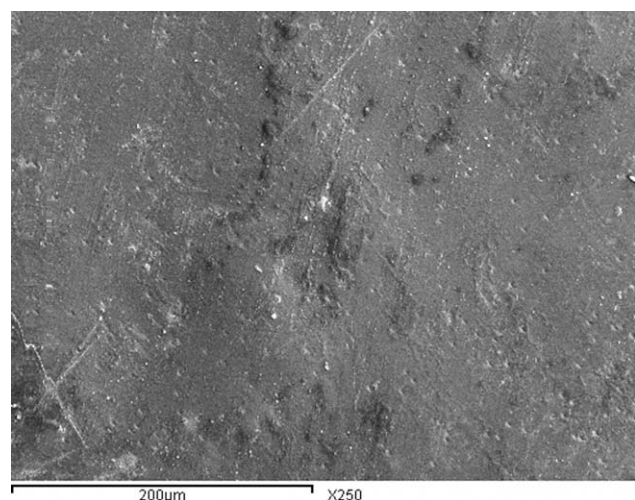


**Figure 5** SEM photograph for blank magnification 250 with magnification 500.

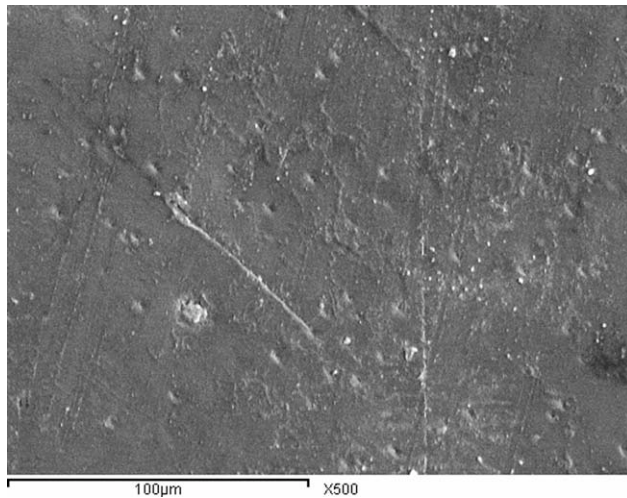
#### Water absorption

Water absorption of the prepared polymer/leather waste composites was determined at different times. The obtained results are shown in Figure 3. Figure 3 showed that water absorption increased with time and reached saturation after 80 min for neat polymer and polyamide loaded with filler wastes. It is also noted that by increasing percent of filler the water absorption% increases, consequently enhances toughness, elongation at break, and impact resistance of the composites compared with the dry one.

In nylon 6 both water vapor and liquid water can be absorbed from the surroundings, where the absorbed water penetrates only the amorphous parts in polymer.<sup>24</sup> The absorption of water has plasticizing effect that may permit relaxations and facilitates molecular chain movement<sup>25</sup> (where that not occurred in dry state), which decreased stiffness and



**Figure 6** SEM photograph for 4% leather waste.

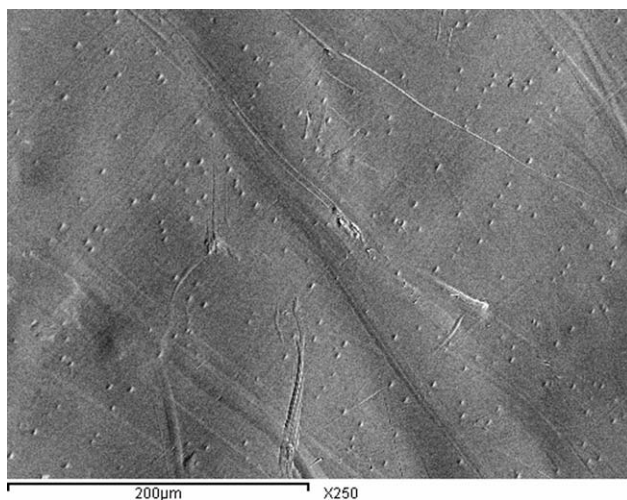


**Figure 7** SEM photograph for 4% composite with magnification 250 leather wastes composite with magnification 5.

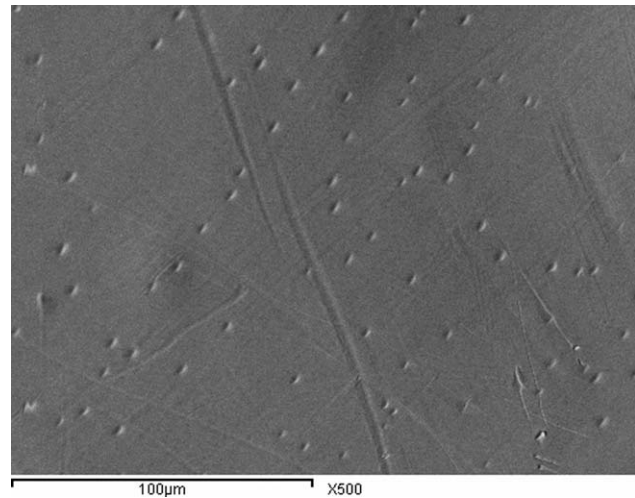
increased flexibility. The increase in water absorption is related to the presence of amide groups  $-NHCO$  in leather wastes and polymer matrix (main constituent), which favors water absorption by forming hydrogen bonding with water molecules.

#### Scanning electron microscopic investigations

Scanning electron microscope (SEM) was used to study the morphology of the prepared samples surface to explore the effect of filler on the surface of polymer composite and its distribution. SEM photographs were taken for neat polymer and samples filled with 4 and 12% of leather waste. The results are shown in Figures 4–9 with magnification 250 and 500. SEM photographs of neat polymer sample show a uniform appearance, while the presence of filler



**Figure 8** SEM photograph for 12% leather waste.



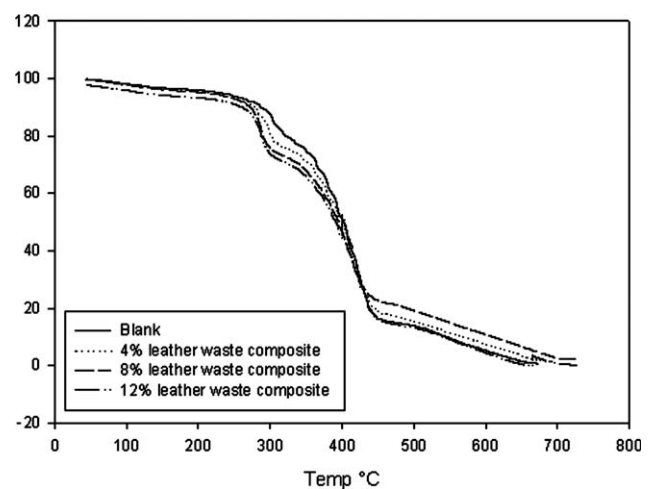
**Figure 9** SEM photograph for 12% composite with magnification 250 leather wastes composite with magnification 500.

formed large particles inclusion which increased by increasing filler percentage from 4 to 12 %.

#### Thermogravimetric analysis

The results of TGA (thermogravimetric analysis) for polyamide and polyamide/leather waste composite are shown in Figure 10.

By plotting Figures of TGA in one graph it is clear that nylon 6 degrades nearly between  $320\text{--}400^\circ\text{C}$ , but in case of polymer composites with filler the degradation appeared at  $290\text{--}400^\circ\text{C}$  this decrease in degradation temperature resulted from decomposition of leather waste at about  $290^\circ\text{C}$ . At range from  $400$  to  $440^\circ\text{C}$  all samples have the same trend after  $450^\circ\text{C}$  the charred residue of composite is higher than the neat polymer.



**Figure 10** TGA of neat Nylon 6 and different composite.

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