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# Sustainable Solid Waste Management in Leather and Textile Industry: Leather & Textile Waste Fibre-Polymer Composite and Nanocomposite - Overview and Review

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## **ABSTRACT**

*Proper disposal methods and solid waste management are necessary for all the processing industries such as leather, textile and chemical industry. In this regard, the present paper reviews in detail about the leather and textile waste fibre-polymer composites and nanocomposites as a viable solid waste management strategy. In the paper, several published papers and patents available in this area are reviewed in detail. This approach adopts confinement of leather or textile waste fibres in a polymer matrix as a composite. Nanocomposites of leather waste fibre and polymer with nano-particle reinforcement have been reported to have enhanced physical and other properties. This would not only solve the problem of the disposal issue regarding leather solid wastes containing leather or textile waste fibres, but also provide versatile composite or nanocomposite materials as "Wealth from Waste Approach". The unique feature of the present analysis and the review paper is that both leather and textile waste management have been covered in the present approach for the first time.*

## **KEYWORDS**

*Leather waste fibre, textile waste, polymer, nanocomposite, waste management*

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## **INTRODUCTION**

Leather processing involves various steps as described earlier, utilizing different chemicals in order to convert putrescible skin/hide into non-putrescible material called leather [1- 3]. Collagen is the main fibrous protein present and mainly responsible for skin/hide formation, having triple helical structure, with different amino acids present in polypeptide chain of single helices. Several molecules of collagen aggregate themselves into hierarchical structures, such as microfibril, fibril, fibre and fibre bundle [4]. Three-dimensional weave of fibre bundles leads to the formation of skin/hide as a matrix, composed of other non-collagenous materials, hair, flesh etc. Hence, skin/hide could act like a semi-permeable membrane, susceptible to physical, chemical and biological treatments – this property is useful and gainfully applied in leather processing.

## Overview of leather processing

Leather processing can be broadly classified into four major steps which involve various unit operations using different chemicals and mechanical operations described as follows:

- I) **Pre-tanning** - removal of non-collagenous materials and preparation of the skin/hide for the subsequent tanning process: soaking, liming, dehairing (M), defleshing (M), deliming, bating, degreasing, pickling, wherein "M" denotes Mechanical operation employing suitable machinery.
- II) **Tanning** - stabilization of the collagen through cross-linking of collagen by tanning agents in order to provide resistance against biological and thermal action (hydrothermal stability).

The most common tanning methods are:

- a) mineral tanning (chrome, titanium etc.) - through co-ordinate covalent bond enabling intermolecular as well as intramolecular cross-links for collagen, and
- b) vegetable tanning (wattle, quebracho etc.) - through hydrogen bonding of condensed tannins of polyphenolic nature with collagen.

After tanning, shaving (M) is carried out in order to adjust the thickness of leather, to be suited for different applications.

- III) **Post-tanning** - to impart required functional properties to the leather
  - a) re-tanning to provide fullness, grain tightness etc. using different synthetic tanning agents known as "syntans".
  - b) dyeing – to impart colour to the leather using dyes
  - c) fatliquoring – to impart lubrication to leather fibres and provide softness; using different oil-water emulsions known as fatliquors [5].

After tanning, setting (M), drying, stacking (M), buffing (M) - finely cutting the tanned fibres in order to get a napped or a velvet feel; carried out as suited for different applications of leather.

- IV) **Finishing** - to provide protective coating on the surface of leather and to provide an aesthetic look by utilizing different finishing agents, such as
  - a) binders - film forming polymers etc.
  - b) pigments - colour giving particles or dispersions - inorganic (e.g. TiO<sub>2</sub>) and organic pigments
  - c) lacquers - protective coat for the finishing film - nitro cellulose (NC) etc.

## Need for solid leather waste management

For every 1000 kg of raw hide processed for leather, only 255 kg of the raw material is converted into usable leather including leather splits. Nearly 745 kg is generated as solid waste in leather processing [6]. Of these, nearly 20–25% are in the form of tanned leather waste such as trimmings, shavings and buffing dusts which pose major environmental concern. As a solid waste management strategy, leather fibres from these solid wastes could be converted into useful products such as composite material along with suitable polymers [7]. A report by UNIDO indicates about 1402.43 tons per year of total leather waste generated for all the leather and leather products industries; for every 11 million tons of raw hides processed, 8.5 million tons of solid waste is generated as per the earlier report by FAO and other reports [8-10].

Typical solid waste generated in a tannery: fleshing - 30%, hair - 2–5%, chrome shaving, chrome splits and leather waste - 20–25%; skin trimmings - 10%; buffing dust - 1%. About 2–6 kg of buffing dust is formed per ton of skin/hide processed [11, 12].

## Characterization of various solid leather wastes

Various solid wastes generated from leather processing industry, such as pre-fleshing waste, limed fleshing waste, shavings, buffing's and leather trimmings have been analysed for their characteristics, such as water content, pH, oils & fats content, nitrogen content, sulphur content (SO<sub>2</sub>), calorific value, and Cr, Fe, Na and Ca content, which was reported earlier for different types of raw materials [9].

Cr content in tanned leather fibre shavings and buffing's typically varies in the range of 11-28 mg/g of leather waste [10, 11]. Leather waste materials predominantly contain chromium in the form of Cr (III), whereas, there is a possibility of presence of Cr (VI), which could be analysed through total chromium and Cr (VI) estimation through suitable chemical analysis methods developed by ISO and IULTCS official test methods IUC 8 & 18, such as [13]:

- I) UV-Vis spectrophotometric method after acid digestion, oxidizing the sample, and with measurement carried out at 540 nm using diphenylcarbazide complexing agent
- II) inductively coupled plasma (ICP) analyser
- III) atomic absorption spectrophotometer (AAS) - while Cr(VI) is toxic by nature, Cr(III) is relatively unarmful. Similarly, significant quantities of textile wastes are generated and composites reinforced with recycled cotton textile waste materials and polymers would also form an attractive option.

## Materials and tools for leather waste fibre–polymer composites

Polymer composites are versatile materials obtained by utilizing various properties of polymers, such as adhesion, thermal stability and easy adaptability for various material processing techniques, along with other materials in question for composite making, such as fibres, glass, wood etc. Such polymer composites are expected to yield enhanced properties. Therefore, a similar approach could be used for making leather waste fibre-polymer composites.

Various polymers available for leather fibre composites are listed below:

- A. Thermoplastics:
  - polyamide (PA)
  - polyvinyl chloride (PVC)
  - polyethylene (PE), polypropylene (PP)
  - polyether ether ketone (PEEK)
- B. Thermosets:
  - epoxy polymer
- C. Elastomers:
  - natural and synthetic rubber (SR)

Various methods and tools for making leather waste fibre-polymer composites are as follows:

- twin-screw extrusion process
- injection moulding
- laminates - composite sheet making

## Processing conditions for leather waste fibres

Processing conditions for leather waste fibres, such as temperature for making composites, could be selected based on the values of shrinkage temperature of various materials used and based on the type of tanning, which are as follows:

Untanned skin/hide waste (raw trimmings etc.) - 60-65 °C

Vegetable tanned leather waste (shavings, buffing, trimmings) - 70-80 °C

Chrome tanned leather waste (shavings, buffing, trimmings) - 85-100 °C

### Nanocomposites from leather waste fibres

Currently available composites from leather waste fibres lack strength properties required for various applications. Therefore, reinforced nanocomposite material from leather waste fibres is useful. In this regard, leather waste fibre and epoxy-based nanocomposites have been prepared by using nano-TiO<sub>2</sub> reinforcement at CSIR-CLRI and reported earlier [7,14]. DSC/TGA of such buffing dust-epoxy polymer nanocomposites exhibit better thermal stability compared to composites alone [7]. Figure 1 shows the image of the scanning electron micrographic (SEM) analysis for the cross-section of the nanocomposite prepared using rubber and buffing dust in the 1:1 ratio with nano-TiO<sub>2</sub> (10 wt %).

These nanocomposites have adequate physical and other required properties as a versatile material that can be used for a variety of applications, such as light weight construction materials, automotive nanocomposite, footwear components, electrical switches etc.

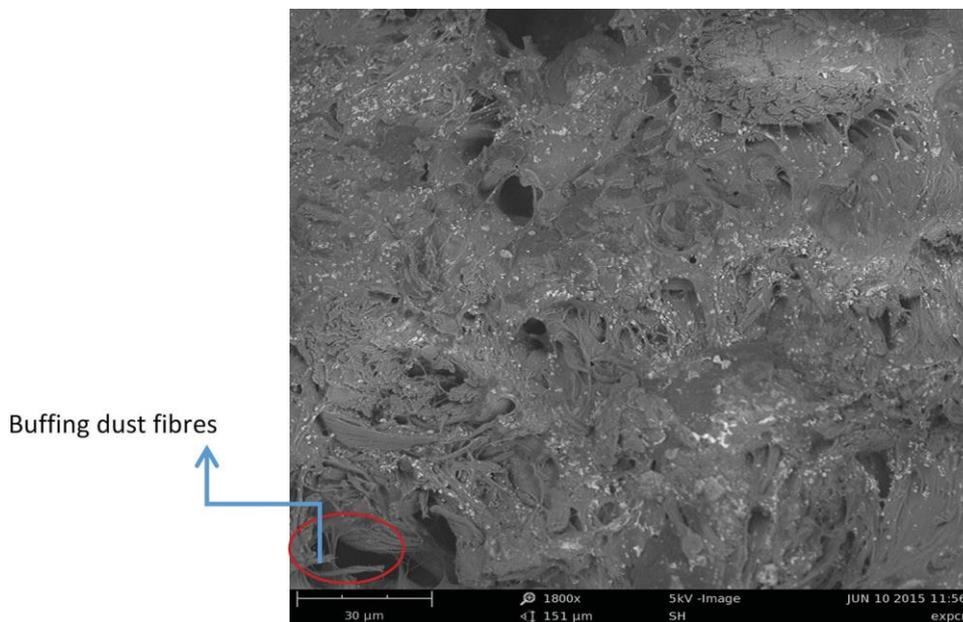


Figure 1. SEM analysis of the cross-section of the rubber-buffing dust nanocomposite (in 1:1 ratio) prepared by using nano-TiO<sub>2</sub> (10 wt %) (magnification: 1800x)

### Various leather wastes generated and their usage

A review on the utilization of solid leather waste has been made earlier [15 -17]. Various methods and products obtained by utilizing various solid wastes generated from leather industry are as follows:

Raw trimmings - collagen based materials, glue, pet foods

Fleshings - fleshing meal

Tanned leather splits - chrome splits or vegetable splits: usually smaller cut portions could be used for leather boards etc.

Shavings - parchment like leather, leather board, composites

Buffing dust - parchment like leather, leather board, composites

Leather trimmings - leather board, regenerated leather, composites

## Advantages and disadvantages of using leather waste fibres in composite/nanocomposite making

### Advantages

Leather waste fibres could be effectively used in composite/nanocomposite making as filler materials in order to provide better composite matrix, porosity, thermal stability, strength properties etc. Certain properties of leather waste fibres could be complementary in nature to the properties of polymer in question for better composite making. Since leather waste fibres are resourced from inexpensive waste materials, using them could add value to the expensive polymers.

### Disadvantages

Since they are sourced from waste materials, which come from various places and different types and process conditions, there is bound to be inconsistency in characteristics and properties of these fibres and the same may reflect in the final product made out of these waste materials.

### Dimensions of leather waste

The dimensions of leather waste fibres, such as shavings, buffing's and leather trimmings, that are obtained, vary depending upon the degree of force applied, or the extent of fibre cutting on the leather in a single feed by using machines like splitting, shaving or buffing machines, or the extent of manual cutting in case of leather trimmings as shown in Table 1. The geometry of each type of leather waste is not confined to a specific geometry; however, it may be assumed that it is one which falls in closer to the specific geometry.

Table 1. Dimensions of leather waste or fibres obtained

S. No.	Leather waste fibres	Dimension (mm)
1	Tanned leather splits	~10 - 30
2	Shavings	~1 - 10
3	Buffing's	~1 - 5
4	Leather trimmings	~5 - 30 cm (for skins)
		~5 - 65 cm (for hides)

In addition, several reports and patents on leather waste fibre-polymer composites are available as follows.

### Earlier reports and patents on leather waste fibre-polymer composites

Picagli et al., (Patent No. EP0089029 A2; 1983,) wherein a reconstituted leather product is produced from fibrillated leather fibres [18]. The highly preferred leather product is prepared by a process which includes dry-chopping pieces of chrome tanned leather, wet-fibrillating the resulting dry-chopped leather so as to realize an aqueous slurry containing the fibrillated leather fibres, mixing the slurry with an ethylene-vinyl acetate co-polymer binding agent, and optionally, a fatliquoring agent, felting the resulting slurry, removing the remaining water to realize a dried felt having 80–90% solids, and finally, pressing the felt at a temperature sufficient to fuse the binder.

Schmidt, (Patent No. US 6,287,639, 2001) wherein the patent relates to composite materials characterized by a substrate and by a nanocomposite which is in functional contact with the substrate and is obtainable by surface modification of colloidal inorganic particles with one or more silanes of the Rx-Si-A4-x [19].

Coulson et al., (Patent No. WO2007047848, 2006) wherein leather composites and the methods of making them that include engineered leather substrates or composites are disclosed [20]. The substrate includes leather, non-leather fibres and a binding agent, and can further include cushioning agents, softeners, processing aids and colorants. A composite can include the substrate and one or more additional layers, such as top coat layers, reinforcing layers and cushioning layers. The substrate and/or the composite can be chemically or mechanically embossed. The leather used to form the engineered leather substrate can be derived from post-industrial and/or post-consumer materials. The non-leather fibres can be organic or inorganic, and the composition can also include inorganic fillers, such as calcium carbonate and clays. Krecke, (Patent No. US 4536430, 1985) wherein a process for the production of a leather base material entails leather waste being divided up into strips or portions by cutting or shearing [21]. The strips or portions are then worked in order to break them up into fine material and individual fibres. The operation of working the strips or portions to cause them to disintegrate may be done by tearing or shredding the strips or portions, or crushing or bruising them. The individual fibres are then separated from the fine material. In order to improve the qualities of the fibre material, an advantageous development of the invention provides that the fibre material is mixed with a plasticizing agent and/or a binder and/or a resin before it is applied in the form of a layer to a surface intended to receive it.

Rajaram et al., wherein the study describes the preparation and characterization of leather particulate-polymer composites (LPPCs) from solid wastes (chrome shavings/buffing dusts) generated during leather manufacturing processes [22]. Nitrile butadiene rubber (NBR), styrene butadiene rubber (SBR) and neoprene rubber were the polymers used at different concentrations. The drawback is that the product is a composite based solely on rubber-based polymers, made without incorporating nanomaterials to get a nanocomposite with improved properties.

Ramaraj, wherein the study describes the possibility of using leather waste as reinforcing filler in the thermoplastic polymer composite, acrylonitrile-butadiene-styrene (ABS), as the matrix, and leather buffing powder as the reinforcing filler to prepare a particulate reinforced composite [23]. The drawback is that the product is a composite based on ABS and leather waste as the filler, and made without incorporating nanomaterials to get a nanocomposite with improved properties.

Ambrosia et al., wherein the study describes the preparation and characterization of polyvinyl butyral-leather fibre composites [24]. The drawback is that the product is a composite based solely on PVB polymer, and made without incorporating nanomaterials to get a nanocomposite with improved properties.

Zeng et al., wherein the study describes the process of synthesizing leather-epoxy interpenetrating polymer networks (IPNs); these IPNs have an approximate epoxy concentration of 25 wt % [25]. The flexural and tensile moduli of the IPNs prepared are equivalent to that of the epoxy resin.

Sutton has studied the production of polyurethane film/split leather laminate (US Patent: US 3713938A, 1970) [26]. Salwa et al. have reported the recycling of chrome-tanned leather waste in acrylonitrile butadiene rubber [27]. Mohamed et al. have made the preparation and characterization of polyamide leather waste polymer composites [28]. Tao et al. have studied about the cleaner Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>/MMT nanocomposite adsorbent based on Al-Zr tanning waste, JALCA, 109, 39-396, 2014 [29].

Babanas et al. have reported about the plasticized polyvinyl chloride filled with leather waste particles [30]. Various studies on both natural and synthetic-rubber-based leather waste composites are also available, such as Garcia et al. on natural rubber/leather waste composite foam: a new eco-friendly material and a recycling approach [31]; Urrego Yepes on the mechanical and rheometric properties of natural rubber composites filled with untreated and chemically treated leather waste [32]; Meşe et al. on the study of effect of chrome-tanned leather scraps in ethylene-propylene-diene monomer rubber [33].

Duan et al. have studied the preparation and characterization of the covalent-integrated polylactic acid and scrap-leather fibre composites, and strength and thermal properties are found to be improved [34].

Joseph et al. have studied the processing and characterization of leather waste-based polycaprolactone (PCL) biocomposites and found that the addition of waste leather buff resulted in the improvement of tensile modulus of neat PCL [35].

A similar study on polylactic acid (PLA) composites filled with waste leather buff has also been made, and it shows the improvement in tensile strength and wet-ability of the composites due to the addition of buffing dust [36].

Madera-Santana et al. have studied the production of leather-like composites using chemically modified short leather fibres that went through chemical modification by emulsion polymerization. The treatment significantly improves the thermal stability of fibres. It also reduces their water adsorption capacity, as a coating of PMMA is produced over the leather surface [37].

Saikia et al. have studied the development of a flexible composite from leather waste and evaluated its physio-chemical properties. Flexible composite sheets were made from dyed trimmings, either alone or in combination with natural fibres in various blend ratios [38].

### **Polymer composites from textile waste**

Textile processing involves various steps, such as fibre making from cotton or synthetic fibres, yarn spinning, weaving or knitting to make fabric, wet processing of fabric (bleaching, dyeing, finishing), cutting, stitching, garment manufacture [39].

Various types of waste, generated from each stage of textile processing, have been analysed earlier, and they mainly comprise of fibre wastes, yarn and fabric scraps and off-spec fabrics [40]. These are classified as pre-consumer textile wastes and account for about 750 000 tons per year in India [41]. The characterization of textile solid wastes has been reported earlier [42].

The morphology of cotton as well as its various properties, such as cellulose crystallinity, the degree of polymerization and decomposition temperature have been reported earlier [43]. Exposure to dry heat above 149 °C causes cotton fibres to decompose gradually, whereas temperatures above 246°C cause rapid deterioration. Dimensions of various textile wastes and fibres vary.

Thermoset composites reinforced with recycled cotton textile residues, which show strength properties, are increased due to the use of thermoset resins (epoxy, orthophthalic polyester and polyurethane) [44]. The mechanical behaviour of hybrid composites developed from textile waste fabrics, such as cotton, jute and glass, showed enhanced tensile and flexural properties [45].

The natural-fibre textile composite engineering, with a focus on natural fibre-polymer composites, has also been detailed in the book [46].

The properties of wood with recycled-textile composite panels have been studied earlier and it has been found that up to 5 % of recycled textiles in the wooden panel could be used without hampering the mechanical properties [47].

The effects of waste fabric properties, such as fabric tightness etc., on recycled fibre length, the spinnability of recycled cotton fibres and the properties of produced yarns were analysed earlier [48]. A similar study on industrial cotton waste recycling, the reclaimed fibre behaviour and quality prediction of its blend have also been studied [49].

The preparation and structural properties of fibrous-materials-reinforced polymer composites along with laminated hybridization and coupling agents has been studied earlier [50].

### **Advantages of using textile waste fibres in composite/nanocomposite making**

The utilization of these huge amounts of cotton and other textile wastes for making possibly useful materials would be beneficial for reducing pollution load on one hand and generating economic value on the other.

Textile waste fibres such as cotton fibres could be effectively used in composite/nanocomposite making as filler materials in order to provide better composite matrix, thermal stability, strength properties etc. Certain properties of textile waste fibres could be complementary in nature to the properties of polymer in question which would allow for better composite making. Since textile waste fibres are resourced from inexpensive waste materials, using them could add value to the expensive polymers.

## CONCLUSION AND WAY FORWARD

Significant amounts of solid leather and textile fibre wastes are generated worldwide, which needs adequate attention and calls for proper solid waste management strategy. In this regard, the present paper analyses in detail the leather waste fibre-polymer composites and nanocomposites as a viable solution to this problem. Several earlier works carried out in this regard, available from published papers and patents, are reviewed. Composites reinforced with recycled cotton textile waste materials and polymers would also form an attractive option. The unique feature of the review paper is that the analyses of both leather and textile waste management have been covered in the present approach for the first time. This approach, as a solid waste confinement strategy, not only solves the problem of the disposal issue regarding leather and textile solid wastes containing leather and cotton waste fibres, but also provides versatile composite or nanocomposite materials as “Wealth from Waste Approach”.

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