Development of Composite Membranes from Silk Waste and its Characterization

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Abstract -The textile industry is the second largest sector of global trade market and has to shoulder responsibilities towards maintaining the environment. Manufacturing of leather products for the fashion is moving towards alarming situation because of extensive nature of the chemicals used and resources utilized. Several alternatives for leather, the so-called artificial leathers are being made, but production of all these are involved with several synthetic polymers and chemicals that are not eco-friendly. It is also notable that the present fashion and international market scenario is shifting towards sustainability. Thereby an idea of structuring a composite membrane as an alternative for leather using silk waste has been materialized in the work. This composite makes use of silk waste and a fermentable organic liquor for the preparation. The basic concept of forming the leather like membrane is fermentation of the silk wastes using organic liquor. The study relates the properties of the membranes formed with various combination of the materials used, time involved and other variable factors.

Key Words: Vegan, Leather, Silk, Silk waste, Reeling effluent, *SCOBY*

1. INTRODUCTION

Leather and the leather industry has been around a long while – there are those who claim it is the second oldest profession in the world. Going back a few millennia, when our earliest ancestors decided that sitting on hard rock was not a soft option, they turned to other materials to create more comfortable seating, as well as warmer bedding and some more acceptable form of clothing to go out in.

Leather is the end product of tanning the rawhide of an animal to make it durable and yet very flexible. Leather is commonly made from cattle hide, although the skins from almost any animal (mammals, amphibians and reptile) including exotic animals like ostriches, kangaroos, pythons and even camels can also be tanned into leather. Leather is used to make a variety of items which includes clothing, footwear, handbag, furniture, tools, sports equipment, etc., that lasts for decades. The leading producers of leather on today are China and India.

The term hide is used to designate the skin of larger animals (e.g., cowhide or horsehide), whereas skin refers to that of smaller animals (e.g., calfskin or kidskin). The preservation process employed is a chemical treatment called tanning, which converts the otherwise perishable skin into a stable and non-decaying material. Tanning agents include vegetable tannins (from sources such as tree bark), mineral salts (such as chromium sulfate), and fish or animal oils. Although the skins of such diverse animals as ostriches, lizards, eels, fish, and kangaroos have been used, the more common leathers come from seven main groups cattle, including calves and oxen sheep and lambs; goats and kids; equine animals including horses, mules, and zebras; buffalos, pigs and hogs; and aquatic animals as seals, walrus, whales, and alligators.

Critics of tanneries claim that they engage in unsustainable practices that pose health hazards to the people and the environment near them. The processing stages of tanneries consumes thousands of liters of water for one hide or animal skin and release toxic liquid waste into the environment that can cause soil depletion and serious health issues on human skin, respiratory system and more. However, recent advancements have helped in reducing the amount of water used by tanneries to reduce the pollution and impact.

2. NEED AND SCOPE OF THE WORK

Animal Leather is one of the most widely traded commodities and highly consumed material in every fashion trend irrespective of seasons and cultures on the global scale. The growth in demand for leather is steadily increasing and is driven by the fashion industry. Apart from fashion, leather is used in furniture, interior design, industrial applications, as well as the automotive industry also demands leather. The leather industry has a place of prominence in the Indian economy due to substantial export earnings and growth.

The animal skins are made as usable leather after several chemical treatments and processes of which tanning is an important process. In tanning process, a higher concentration of chromium is commonly used which is a heavy metal, that is toxic and hazardous to human health and other eco system. Effluent of the leather making process is highly polluting and non-eco-friendly. The effluent discharge of the tanneries seems to be regulated but in the real time there are many complications in managing the discharge standards that increases the price of the product and most tanneries could not keep up to the mark in the effluent discharge.

The global leather goods market size was valued at USD 394.12 billion in 2020 and is expected to grow at a compound annual growth rate (CAGR) of 5.9% from 2021 to 2028. The market is mainly driven by rising consumer disposable income, improved living standards, changing fashion trends, and growing domestic and international tourism. The rising demand for contemporary designs offered by prominent international brands, such as Giorgio Armani, Burberry, Prada, Dolce & Gabbana, Louis Vitton etc., is driving the demand for various leather goods including apparel, footwear, and accessories.

India is the second largest producer of leather after china and holds comprehensive position in leather export as second largest exporter of leather garments, third largest exporter of Saddlery & Harness and fourth largest exporter of Leather accessories Goods in the world. The export of Leather and leather products from India was to the tune of USD 5.26 billion during 2022-2023. Annual availability of leathers in India is about 3 billion sq.ft. India accounts for 13% of world leather production of leathers. Indian leather trends and colors are continuously being selected and awarded at the MODEUROPE Congress, A renowned European platform for trends and fashion. India is the second largest global exporter of leather apparel products and accounts for 8.03% of total Indian leather exports (2020-21), accounting for export value of USD 40 million, besides the domestic market.

Market for Leather apparel and clothing being huge and the gradual rise in number of people who move towards veganism leaves a space for a product that can replace the leather will all sustainable properties but not made from animals. The number of people who choose vegan products in the western countries is increasing in a constant rate. The people who choose to be vegans are hesitant to use leather products made of animal skin and they have shown preference to alternative products. But unfortunately, there is no alternative product that is similar to leather, which is eco-friendly. This leaves room for the development of new product made from sustainable sources that can replace the leather which provides a leather like feeling which will be much better than leather and will be bio–degradable, which is environmentally friendly.

With incorporation of silk fiber, the newly developed clothing will be more appropriate for cold weather applications also. With the estimated properties, the vegetable leather will fulfill and replace not only the leather requirement of the vegan market but also will be a competitor for a higher global market share of animal leather apparel.

Objectives

To develop an eco-friendly, durable and suitable replacement for animal leather using silk waste, to be used for apparel in order to gain export market.

To appraise the performance of the product with reference to thermal conductivity and thereby to improve the performance by further product development to suit targeted export markets.

3. MATERIALS

Silk waste

The Silk cocoons undergo various processes viz., reeling, twisting, weaving and dyeing where the raw silk filaments are extracted from the cocoons and subsequently converted into fabrics and products. A hefty amount of waste is generated at every stage of production of silk, especially during reeling, where the Silk filaments are extracted by combining numerous ends of the cocoons together to form a single filament strand for a desired denier. The processes involved during reeling are cocoon drying, sorting, deflossing, cocoon cooking, silk reeling and re-reeling followed by packing as books.

Silk Waste generated during the reeling process depends on the type of cocoon and the type of reeling machinery. As mentioned in the Fig. 1, during the cocoon sorting process, defective and inferior cocoons are identified that are below the required standards. These are segregated and usually accounts to about 5-8%. These defective cocoons are used for the production of low-grade raw silk Cottage basin and Charka units or they can be converted to Silk sheets in case of ARM units.

Flow chart of silk reeling

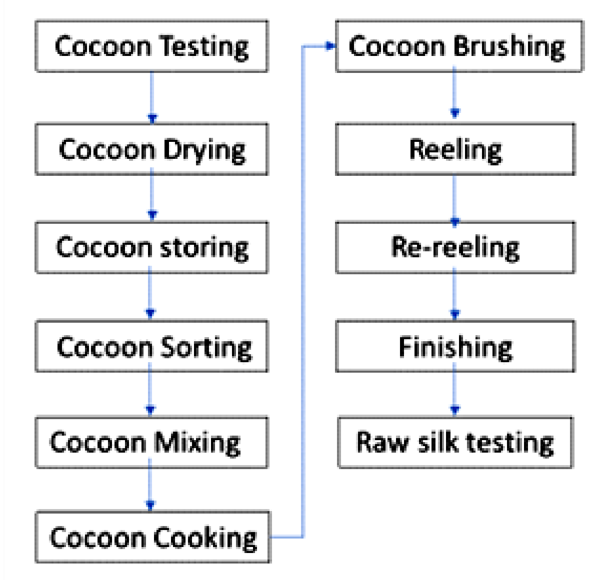

Fig. 1: Silk reeling process

Wastes generated during reeling process

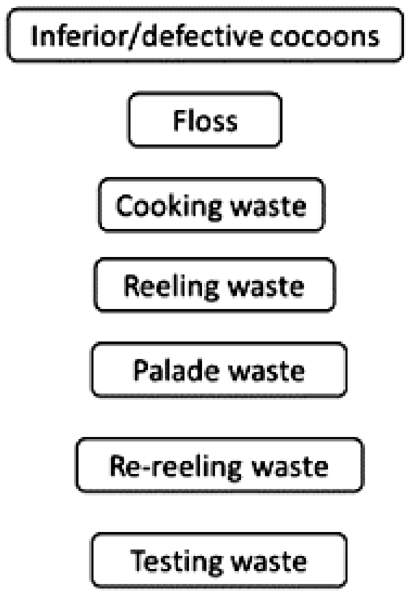

Fig. 2: Wastes generated during Silk reeling process

During the mulberry silk reeling process about 12% of silk waste is generated that includes pupae waste, floss, cooking waste, palade waste, basin waste and re-reeling waste. Out of these, pupae waste is used for fish and poultry feeds whereas palade waste are used for sheet making along with some quantity of silk filament wastes. The remnant silk filament wastes are disposed off for a mere sum of money for various applications. This work uses these said remnant waste for the membranes making technique. The silk filaments being well known for their strength and other physical properties like elasticity and modulus, it can very well suit to be used in composites as reinforcements, giving the built-in strength of the material.

Effluent of silk reeling process

Silk reeling is a wet process technique where the cocoons are first boiled in water for about 45-90 minutes depending on the type and toughness of the cocoons. During this cooking process, a certain amount of the surface protein of the silk fiber, the sericin is dissolved in the water where the cocoon shell softens and the filaments are detached from one another. The cocoon cooking is usually carried out in the industries until certain degree of softness is achieved and individualization of the filaments are achieved. The effluent from this process has significant amount of dissolved protein-Sericin, about 1% of the weight of the cocoons. Further in the subsequent process, the cocoons are handled in hot water troughs, where a part of sericin from the cocoons are further dissolved. These waste waters are disposed off by the industry as effluents as there are no appropriate or commercial methods to treat the industrial effluents as the industries find it expensive to treat these waste water.

Further, during the wet processing techniques on silk, viz. Bleaching and dyeing, it is mandatory for the silk material to undergo the de-gumming process which is the removal of silk sericin from the silk fibroin. Speaking about the characteristics of these proteins, the silk sericin is quite amorphous and can be hydrolyzed easily at elevated temperatures, whereas, the silk fibroin is found to be crystalline and left behind after the sericin is hydrolyzed and removed. With the said de-gumming process the silk sericin is hydrolyzed and removed enabling the further dyeing processing an effective manner. The poor colour fastness on silk is mostly because of the sericin from the silk fibroin is not completely / properly removed in the de-gumming process. The effluent from this degumming process is to contain 22-25% of dissolved sericin on the weight of raw silk used for degumming. Even though the dyeing effluents can be processed effectively through the modern Effluent Treatment Plants (ETP), there are two influencing factors, viz. Silk industry especially weaving along with other allied processes are being more un-organized and processes a few kilo grams of material daily. With this scenario and the practices followed, the silk processing sector could not install full-fledged ETP which is not cost effective. Secondly, the removal of sericin from the effluent is not easy that can be carried out from a small scale ETP. Removal of sericin may require a dedicated ETP which all silk dyers cannot afford.

With this described situation, the silk effluents are commonly disposed off without treating that has significant quantity of protein which will be utilized as a raw material that contributes to the matrix of the composites.

SCOBY

SCOBY stands for Symbiotic Culture Of Bacteria and Yeast. It's a cellulose based active ingredient used in the fermentation especially kombucha tea. It is created by simultaneous fermentation of Lactic Acid Bacteria (LAB), Acetic Acid Bacteria (AAB) and yeast on the same and suitable substrate, which is the liquid sugars combinations. Subsequent to the activation of the bacterial culture, the *SCOBY* serves as a base/substrate for the yeast and bacteria, allowing them to transform the brewed tea and mixture into kombucha. The *SCOBY* plays a crucial role in the transformation process of kombucha as it facilitates the fermentation by providing a suitable environment for the yeast and bacteria to thrive. As the fermentation progresses, the *SCOBY* consumes the sugars in the tea, producing acids, enzymes, and other compounds that contribute to the unique flavor and properties of kombucha. During the said natural fermentation process, the *SCOBY* forms a bio-film layer on the fermentable layer.

Fig. 3: Active SCOBY liquid

Various studies have proved that the bacterial mixture held in the *SCOBY* is not only capable of consuming the sugars but they could more effectively consume the protein material and flourish. Further, with the availably of protein the bio-film layer formed is observed to be thick to ten milli-meters and tough. With the available protein content in dissolved form, the bacterial culture can actively and easily consume the protein and the film formation is quick, as the protein available is already hydrolyzed that can be easily digested by the bacteria.

4. EXPERIMENTAL METHODS

Leather apparel are comparatively more functional than regular clothing products. Leather products are often preferred on cold weather clothing and as wind cheaters, besides fashion and accessories. Experimental design of the product inculcates the use of silk industry effluent which are dumped, unprocessed and waste fibers from silk processing industry. The silk filaments sourced is opened, cleaned and washed with detergents to remove the impurities. Then the filaments are converted to tuft of length between 15-20 cm. The fiber content of the silk is essential for the process of sheet formation. Cleaned silk, silk reeling/de-gumming effluent and *SCOBY* is added in specific proportion. The formulated recipe is made up as an emulsion with silk fibers as reinforcement, sericin water/effluent as matrix and *SCOBY* for sheet forming agent. The viscosity of the matrix complex is maintained at the persistent level so that the bio-film /sheet can be formed with the matrix complex. The recipe is then laid in sheet forming tray with specific thickness as required. The mixture is then left for sheet formation for 7-14 days depending on the thickness of the sheet required.

Subsequent to the sheet formation, wet sheets are then subjected to moisture extraction and drying without compensating the texture and flexibility of the material. This is achieved by slow drying at low temperature and prolonged time. The dried sheets thus obtained are heat cured at 80°C for shorter duration and is subject for physical and comfort testing. The recipe is further optimized to reach as satisfactory level of test results. The sheets obtained from the finally optimized recipe is garmented and the application of the sheets for apparel has to be evaluated. Further optimization thus required is been implemented in the final recipe. The sheets that are made with the prominent and proven recipe are fused with resin embellishments to give the leather patterns as required to meet the fashion trends.

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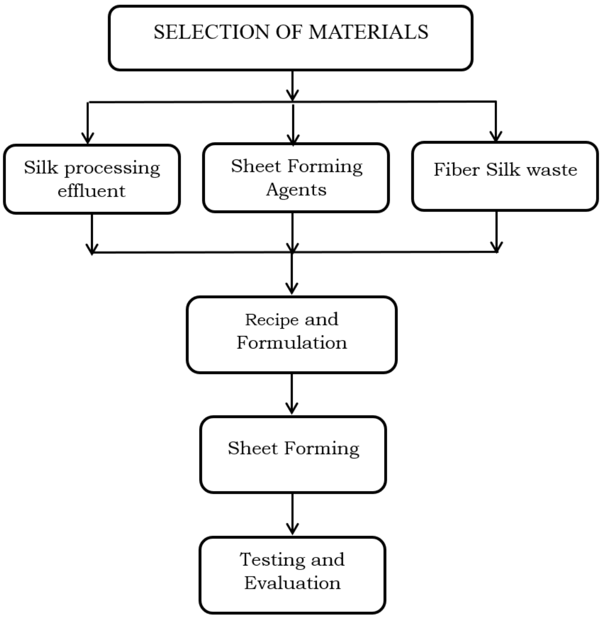

Fig. 4: Process flow for sheet making

Recipe

Various proportion of the said materials were combined and experimented, viz. Silk waste : silk reeling effluent : *SCOBY*, always constituting to 100 parts, where silk filaments/fiber wastes ranges as 10, 20 and 30 parts, *SCOBY* liquid extract ranging in 10, 20 and 30 parts and remaining constituent parts are equalized to 100 parts with effluent water of silk reeling that ranges from 40-80 parts accordingly. Further to these there are other variables like % w/w of sugar (1-3%) being added to the mixture and duration of fermentation (7-15 days).

Table 1: Experimental trials - recipe list

Silk waste- Parts (a)	reeling effluent water- parts (b)	*SCOBY Parts(c)*	Total Parts (a+b+c)	Sugar (w/w)	Thickens of the sheet	Duration of fermentation/ sheet formation
10	80	10	100	Trials with 1%, 2% and 3% with each composition	Approx. 1cm	7, 10, 12 and 15 days
20	70	10	100			
30	60	10	100			
10	70	20	100			
20	60	20	100			
30	50	20	100			
10	60	30	100			
20	50	30	100			
30	40	30	100			

5. RESULTS AND DISCUSSION

On primary study, the influence of the change of the recipe with reference to the sugars, thickness and time was studied to standardize the passive and active parameters. With the passive parameters viz., silk waste been accessed the effects of the active materials like *SCOBY* and Silk reeling effluents could be easily standardized and the effects and influence was observed and determined. Pictures of some of the samples are given below.

Fig. 3 & 4: Samples with minimum silk reeling effluent and low sugar content

The observation from the experimental trials shows that there is a direct correlation between sheet formation factor and the time. The initial sheet layer is formed at seven days but it is more or less incomplete. In the initial days from one to five, the sheet formation is very low which signifies the *SCOBY* content/concentration has not reached to the sufficient level. Since the micro-organism culture is on exponential growth, the after fifth day, the *SCOBY* culture significantly dominates and that results in sheet formation. Subsequently, the grown is witnessed by the sheet formation from the seventh to twelfth day in most of the samples. Some samples, especially with low sugar content and / or low content of effluent reeling water have shown no development after eight-ten days. This observation signifies that the protein content from the reeling effluent is actively consumed the micro-organisms. Further, it is observed that the sheet formation has stopped after fourteen to fifteen days which marks that the growth of micro-organisms has stopped because of the deficit of nutrition.

Fig. 5, 6 & 7: Sheets formed with customized and adapted recipe

The change of silk waste in the mixture also effectively contributes on the quality of the sheets formed. It was identified that the sample trails with minimum volume of silk waste tend to tear off during the removal from the moulds/trays. Moderate volume of silk waste, i.e. 20 parts of the total mixture tend to stay intact during the removal process but still weak which could not withstand the normal material handle. The highest concentration of silk waste with 30 parts of the total mixture was observed to be good in normal material handling process with good bending properties and soft handle. But it is inevitable to inform that material's strength is not up to the limit where it can be tested using laboratory instruments. The strength has to be significantly increased which may be possible by appropriately changing the material ratio.

Fig. 8: Sample that has been set on fermentation for 21 days.

Concentration of the *SCOBY* mixture doesn't have direct effect on the sheet formation. But the indirect effect of the *SCOBY* concentration is that the time required for the sheet formation. This leads to the understanding that with low parts of *SCOBY* liquid, the concentration of the concerned micro-organisms is less and it takes about three to four days to reach the level of concentration from the other higher concentration samples. This symbolizes that the sheet formation is delayed with the lower parts in the mixture. Further trials were undertaken for reduced concentration of the micro-organisms with one part and five parts. It was observed after three to four days that there is fungus formation in the mixture. With this observation provided insights that lower concentration of the *SCOBY* is been dominated by the growth of other unwanted microorganisms that suppresses the activity *SCOBY*. So, it is recommended to possibly have higher parts of *SCOBY* for better results and invariably, the higher parts of *SCOBY* do not have any adverse effects.

Influence of sugars are inevitable in micro-organism culture that has been proven through various literature and researches. The experiment trials with 1-3% w/w of sugars have shown distinctive results. But, on the other side, these experiments could not prove the effect of sugars on a direct note. This is because the mixture always contained a protein part which has assisted the culture of the micro-organisms. This can also be understood that the deficit of the sugars are complemented and compensated by the protein content in the mixture. As already discussed, the sheet formation was incomplete in the samples where both the sugar and protein content were low. This signified that the protein content and sugar content in the mixture are complemented by each other and rationally compensated when-ever necessary.

Fig. 9 & 10: Samples with minimum SCOBY content

Further, time for fermentation is an important factor irrespective of the contents in the mixture.

Invariably, the samples with lower concentration of the micro-organism culture requires more time to reach the required threshold concentration for sheet formation and when the initial concentration the micro-organism culture is more the process is three to four days faster. On the other side, when the concentration of the micro-organism culture is more than threshold required, there is no effect, that could be observed. Moreover, some samples were set aside to study the effect of time. It was observed that after 21 days, the samples tend to dry and lose the flexibility. After 25 days, the samples tend to be brittle and rough which signifies the loss of moisture content.

6. CONCLUSION

This study concludes that the sheet formation on this method is effective and the influence of various parameters has been studied under various factors. This technique needs more refinement where the samples can be tested for fabric/leather parameters under laboratory conditions. Moreover, the post treatment and curing of the samples have developed and the effects to be studied. Since the samples lose moisture content in due course of time a mechanism similar to lamination using natural resins may be developed to stop the moisture liberation and hold the material soft. Subsequent to the refinement and moderating the process, techniques and the recipe, the material should be tested under laboratory for physical parameters. Chemical react-ability shall also be studied in the later part besides test for skin compatibility and comfort properties. With all parameters under study being satisfied, garmenting may be attempted.

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About CSTRI

Central silk Technological Research Institute (CSTRI) is the only research institute in the country dedicated to the Research & Developmental activities related to silk technology. CSTRI was established in the year 1983 by the Central Silk Board, Ministry of Textiles, Govt. of India. Till then, silk technology had only the status of a division in the sericultural research institutes in the country. Appreciating the need for a greater thrust on the demand side of the silk industry, the establishment of CSTRI was the first step in the right direction. Today, CSTRI is recognized as one of the Textile Research Associations in the country by the Government of India.

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