Lignin Based Colorant: Modified Black Liquor for Leather Surface Coating Application

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Abstract

Nowadays, much research is focused towards the development of a value-added products from industrial waste. In this concern, the preparation of pigment colorant with good covering power from the paper and pulp industry waste is less explored within the leather world. The paper and pulp industry generate huge quantity of waste, which is commercially known as black liquor. In order to prepare the pigments with good covering property the black liquor was acidified, and the insoluble organic part of black liquor was used for pigment application. In this work, the structural characterization of the prepared pigment products was analyzed by FT-IR, TGA, DSC, BET, SEM and DLS. Further sol-gel method was employed for the preparation of pigment formulation using the insoluble lignin obtained from the black liquor. The applicability of isolated insoluble as brown pigment was evaluated by using it as pigment for leather surface coating. The color characteristics of the pigment coated leather and checkered card were analyzed by using CIELAB color measurement. The results obtained clearly confirm that the insoluble lignin has potential application as a brown pigment in leather finishing application and is compatible with various auxiliaries employed in leather finishing. Utilization of the prepared brown pigment in leather finishing resulted in upgradation of finished leather through excellent surface covering and in addition, no overloading of grain was observed. Thus, this article provides an approach for converting waste black liquor from paper and pulp industry into a value-added material for pigment application.

Introduction

Leather finishing comprises surface coating of leather with dyes/pigments bound in an organic or protein medium. In that way qualities of leather are enhanced by means of covering the surface defects present in the hides/skin. Specially the preparation of organic pigments from industrial waste for leather finishing pretend to be challenging due to the existence of difficulty in product designing. Considering the rapid industrialization, there has been a generation of huge quantity of wastes, both in the form of solid and liquid, in industrial sectors such as sugar, pulp and paper, fruit and food processing, sago/starch, distilleries dairies, tanneries, slaughter houses, poultries, etc.[1] Despite requirements for pollution control measures, sometime these wastes are generally dumped on land or discharged into water bodies, without adequate treatment, and thus become a large source of environmental pollution and health hazard. However, depending on the waste's characteristics, direct discharge may cause unacceptable environmental harm.[2] Researchers worldwide are working on providing suitable solutions to sustainable minimization of the environmental problems associated with the effluent of paper and pulp industry, well known as 'Black Liquor.' The major constituents of black liquor are lignin, cellulose, hemicellulose, molasses, etc. [3-4] Paper and pulp industry alone produce nearly 50 million tons of black liquor. The black liquor finds use as raw material for synthesis of biofuels and lignin sub-structures.[3, 5-6] Utilizing the waste black liquor is of great environmental and economic importance. Lignin, a component of the paper and pulp industry waste (black liquor), is a poly-dispersed polymeric material made mainly of phenyl propane units such as coniferyl alcohol, sinapyl alcohol, and p-coumaryl alcohol.[7] Conventionally, lignin and its derivatives find application in the preparation of activated carbon, fillers, dyeing agent, carbon fibers, sorbents and motor fuels.[8] Reports are already available on the preparation of tanning agent for leather processing from degraded Kraft lignin,[9,10] which involves sulfonation of the black liquor followed by formaldehyde condensation. It is also reported that chemical oxidation and hydrogenolysis of pulp wastes yields monophenolic aldehydes, ketones and other derivatives.

Oxidation of these phenolic compounds resulted in colored products containing either dark brown or black color. Formation of such colored products will provide the way for using this product as colorant for pigment application. Pigment is a

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material that changes the color of reflected or transmitted light as the result of wave length-selective absorption. Pigments are used in coloring paints, inks, plastics, fabrics, cosmetics, food and other materials. Pigments are dry colorants, ground into a fine powder and are stable in solid form at ambient temperatures. This powder is then added to a binder, which is relatively a neutral or colorless material that suspends the pigments and provides required adhesion towards the leather substrate. According to chemical classification pigments can be classified into either organic or inorganic. In 2006, about 7.4 million tons of inorganic, organic and special pigments were marketed worldwide.[11] After the advent of synthetic pigments there has evolved various classes of pigments that are suited to particular type of industries.

The majority of the organic pigments are chemically synthesized. Raw materials can include coal tar and petroleum distillates that are transformed into insoluble precipitates. Traditionally, organic pigments are used as mass colorants.[12] In recent years, the organic pigments are used for hi-tech applications that include photo reprographics, optoelectronic displays and optical data storage. In the present study, degraded insoluble lignin was separated from black liquor by acidification and the insoluble organic portion was used as brown pigment for surface coating of leather. The pigment obtained was thoroughly characterized by using various instrumental techniques. Preparation of pigments from industrial wastes would not only help to solve important environmental concerns but would also expand the raw-material base for production of various colored organic pigments.

Materials and Methods

Black Liquor (Industrial Waste) was collected from a commercial paper and pulp industry in Erode, Tamil Nadu, India. Sulfuric acid (98%) was purchased from Hi Media Laboratories Pvt. Ltd. Commercial brown pigment (PP18024) obtained from STAHL (P) Ltd. Deionized water was used for the analytical experiments.

Separation of Lignin Based Pigment from Black Liquor

The insoluble lignin was separated from black liquor by precipitating it with sulfuric acid (Concentrated 98%). The initial pH of the black liquor was 13.0 and the pH was reduced in a control manner from 13.0 to 7.0 by the slow addition of acid. The separated lignin was filtered and then the precipitated lignin was washed with water several times to eliminate impurities. The obtained filtrate was used as filling cum retanning agent.[13] The separated lignin contains brown particles was thoroughly characterized and compared to that of standard lignin.

Characterization of Separated Lignin

FT-IR Analysis

FT-IR spectrum was obtained using an ABB MB 3000 spectrometer at room temperature. All spectra were taken at 4 cm^{-1} resolution, averaged over 31 scans in the range of 500 to 4000 cm^{-1}. Separated lignin and standard lignin were mixed with potassium bromide in the ratio of 2:100 (IR grade KBr was used as scanning matrix) to make nearly transparent and homogeneous pellets and then taken for FT-IR measurement. The final spectra were recorded after subtracting the background spectra of KBr.

Thermogravimetric Analysis and Differential Scanning Calorimetry

Thermogravimetric analysis (TGA) and Differential scanning calorimetry (DSC) measurements were performed using TAQ 50V20.6 build through gravimetric analyzer. TGA measurements were performed in platinum crucible from 50-800°C with a heating rate of 20°C min^{-1} under nitrogen atmosphere.

Bruner Emmet Teller (BET) Surface Area Measurements

The specific surface area of the separated lignin was determined by the adsorption isotherms of N_2 at 77 K by using an ASAP 2020V4.01 (V4.01) BET surface area analyzer. Samples were dried in an oven at 120°C overnight and degassed at 150°C for more than 30 min prior to the adsorption measurements.

Scanning Electron Microscopy

The separated lignin was oven dried at 90°C for 1 h. The samples were rinsed with methanol and sputter-coated with gold to avoid possible contamination. Scanning electron microscopic (SEM) characterization was performed using PhenomPro micrograph analyzer.

Table I
Finishing formulation prepared from lignin based pigment.

S. No	Component	Parts of emulsion
1	Separated Lignin	60
2	Soft resin binder	70
3	Medium soft resin binder	70
4	Soft protein binder	60
5	Soft polyurethane binder	60
6	Wax emulsion	20
7	IPA	40
8	Water	625

Dynamic Light Scattering Measurement

The particle size distribution of the separated lignin was determined by using dynamic light scattering instrument (Zetasizer nano, Malvern instruments U.K) at 25°C. Initially, the separated lignin was dissolved in THF and then sonicated for 10 min before the analysis. All the experiments were performed in triplicate and average was taken.

Pigment Formulation for Leather Finishing Application

The pigment formulation was prepared by mixing the separated lignin, binder and emulsion in a particular ratio and made up with water as shown in Table I. The prepared pigment formulation was evaluated for its stability and it was used in leather finishing application.

Mass Tone or Hiding Power of the Pigment

The precipitated pigment was grounded and separated to various sizes and was analyzed for their mass tone/hiding power. The hiding power was evaluated by coating on an opacity chart at a thickness of 150 µm. The CIELAB 1976 method of determination of L, a*, b*, c and h was employed to determine the hiding power of the pigments.[14]

Characterization of the Finished Leather

The leather samples coated with the prepared pigment formulation was tested for light fastness after conditioning according to IS 6191 e 1971 (LF: 4).[15] The samples were exposed to Xenon arc light under prescribed conditions for 20 h along with the dyed blue wool standards. The black panel temperature was maintained at 63±1° C and the relative humidity was 30±5°C.

The dry and wet rub fastness of the pigment coated leather was determined as per standard procedure[16] using Crock meter.

The leathers before and after finishing with the prepared pigment formulation were subjected to reflectance measurements using a premier color scan SS5100A instrument. Color values (L, a*, b*, c and h) were recorded, where L represents lightness, a* represents the red and green axis and b* represents the yellow and blue axis, h represents hue, c represents chromaticity.[17]

Results and Discussion

The black liquor from the paper and pulp industry was acidified to pH 7.0 using sulphuric acid and the insoluble lignin was separated. The solid content of the black liquor has been determined to be 59±2% (wt/vol). The separated insoluble lignin contains 15-20% (wt/wt) of the total solid content of the black liquor. The separated lignin appears dark brown color, which is similar to that of standard lignin purchased from Sigma Aldrich Co. The separated lignin has been analyzed for physical and chemical properties by using various instrumental techniques and the results have been compared to that of the commercially procured lignin.

Characterization of the Separated Insoluble Lignin from Black Liquor

FT-IR analysis

The FT-IR spectra of both separated and the standard lignin are shown in Figure 1. As compared to standard lignin, the insoluble lignin separated from black liquor has similar characteristic peak with major functional groups. The strong and broad peak at 3422 cm^{-1} is corresponds to characteristic peaks of OH groups or phenolic compounds. Similarly peak at 2939 cm^{-1} is assigned to–CH_2 symmetric and asymmetric stretching frequency of methyl or methylene groups of side chains. Moreover, the two bands at 1615 cm^{-1} and 1510 cm^{-1} are characteristics peaks of benzene ring due to the stretching vibrations. The additional bands at 1212 cm^{-1} and 614 cm^{-1} present in the spectrum of modified black liquor is attributed to -C-S stretching.[18] Confirmation of OH groups, methyl, and methylene groups both in the lignin as well as separated insoluble lignin confirms the presence of lignin component in the insoluble separated from black liquor.

TGA and DSC Analysis

Thermogravimetric analysis (TGA) and differential scanning colorimetry (DSC) techniques have been employed to determine the loss of weight of the samples with respect to increase in temperature, which in turn indicates the thermal stability of the samples. The thermal decomposition of separated and the standard lignin has been determined by TGA analysis (Figure 2) under N_2 atmosphere. The initial decomposition temperature starts at 74°C and 145°C, respectively for the separated and

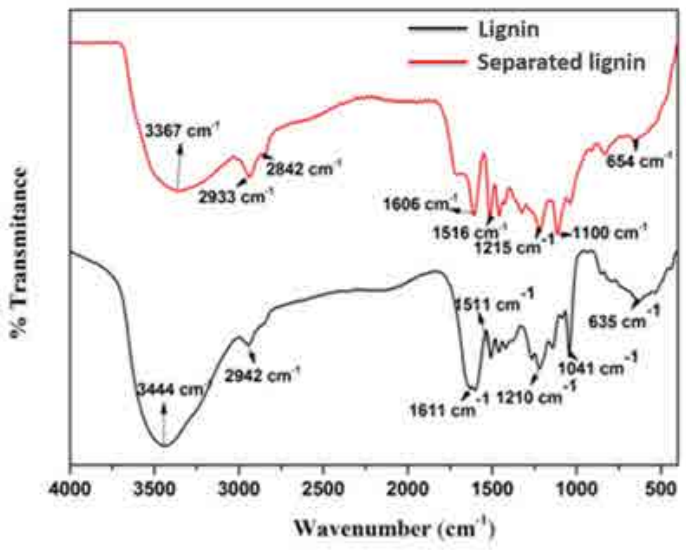

Figure 1. FT-IR Spectrum of the separated and standard lignin.

standard lignin. The weight loss of separated lignin and standard lignin has been observed to be less than 20%. Thermal degradation of the standard/separated lignin compounds has started above 100°C and has been found to be stable up to 200°C. It can also be seen from the Figure 2 that the decomposition of aromatic rings occurs above 400°C, because of the breaking of the bonds between monomeric units of lignin, leads to release of phenol.[19] In DSC, differences in heat flow are recorded as a function of temperature, degradation curve depends on the behavior of the sample as a result of endothermic or exothermic events taking place during the treatment. The initial decomposition has been attributed to impurities present in the system. Degradation profile of the separated and the commercial lignin has been provided in the Figure 3. From the degradation

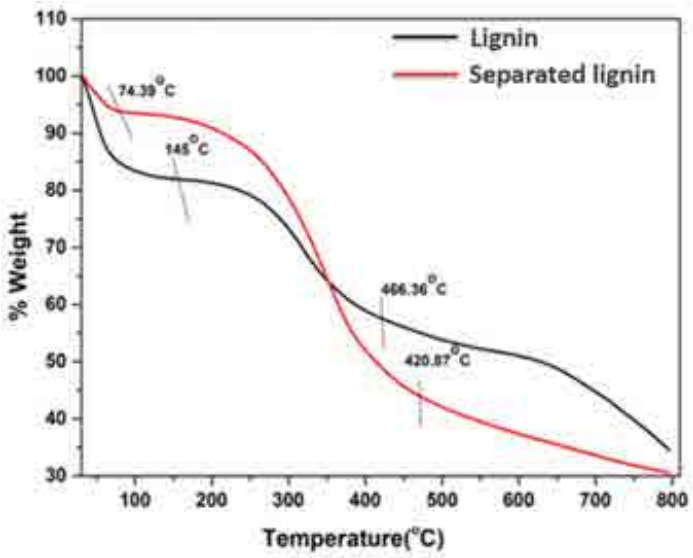

Figure 2. TGA curve of the separated and standard lignin.

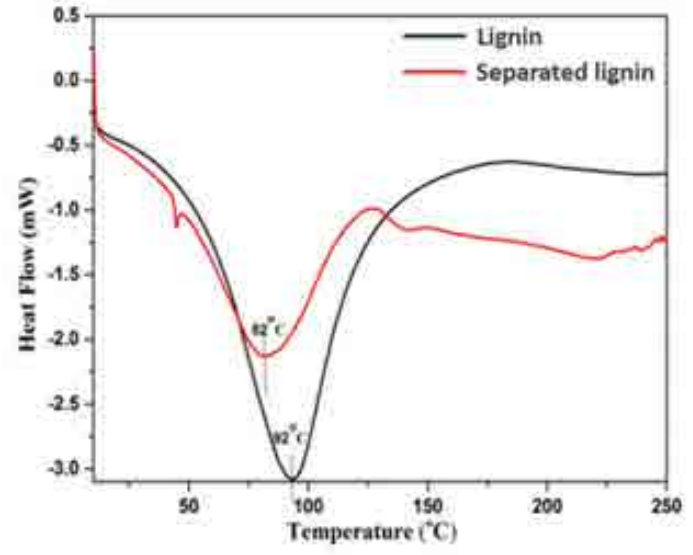

Figure 3. Differential Scanning Calorimetric profile of the separated and standard lignin.

profile, it could be observed that the melting point of separated and the commercial lignin are 82°C and 92°C, respectively. Reduction in melting point for the separated lignin as compared to standard lignin could be due to the presence of neutral salts formed during acidification process.

BET Surface Area Measurement

The surface area and pore size distribution analysis of the separated lignin has been carried out. From the measurement, the BET surface area of the separated lignin has been determined to be 1.5057 m^2g^{-1}. Surface area is an important parameter for choosing the compound for pigment applications. In this concern, it was inferred that the existence of suitable surface area of insoluble lignin after grinding revealed that the separated lignin could be efficiently used as pigment. The total pore volume of the prepared pigment has been found to be 0.0038 cm^3g^{-1}. The significant interaction between the substrate and the adsorbate molecules can be achieved if the surface area of the adsorbate molecules is larger. Hence due to the presence of appropriate pore size and large surface area, the separated lignin can be utilized as pigment for coating application.

Scanning Electron Microscopic (SEM) Analysis

SEM analysis of the separated lignin has been carried out and the images are shown in Figure 4a. It can be seen from the surface of separated lignin that the particles were uniformly dispersed with small aggregation. In addition, particles of lignin based pigments exhibit spherical particles heterogeneously distributed with average size value of 600 nm. The presence of spherical particles with optimal size favors the uniform coating over the leather surface. It could be observed from the Figure 4a that the separated lignin has uniform structure over the entire surface. Also, it could be observed that the separated pigment appears to be agglomerated together as though they are glued together by a film like structure. In order to determine the dispersing property of the prepared pigments, the hydrodynamic diameter of the pigment particles dispersed in solvent medium was studied and shown in the Figure 4b. The hydrodynamic diameter of the pigment particles reveals that the particles are distributed in broader range with average size diameter of 447 nm, which can provide uniform coating over the leather substrate. Further the negative surface potential ("-27±0.7mV) of lignin particles shown in Figure 4c ensure the stable suspension in solvent medium.

Mass Tone or Hiding power

To further demonstrate the potential application as pigment, the separated lignin has been evaluated for mass tone or hiding power. Test methods for mass tone have been standardized as per procedures adopted by exterior coating (paint) industries.[14] A better mass tone or covering power could be obtained if the particles are in uniform size. In order to attain uniform size, the separated lignin was ball milled, sieved (0.25mm) and dispersed

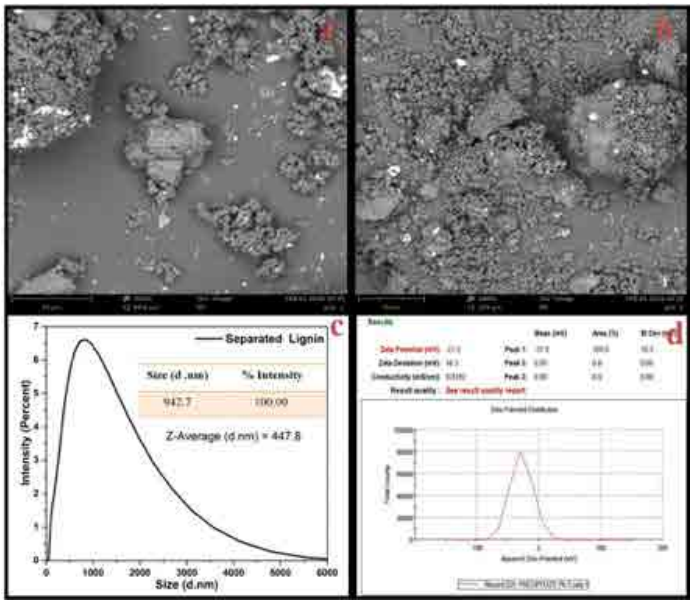

Figure 4. Scanning Electron Microscopic images (a, b), hydrodynamic diameter (c) and their corresponding surface potential (d) of lignin based pigment.

Figure 5. Mass tone/hiding power of the lignin based pigment coated checkered card.

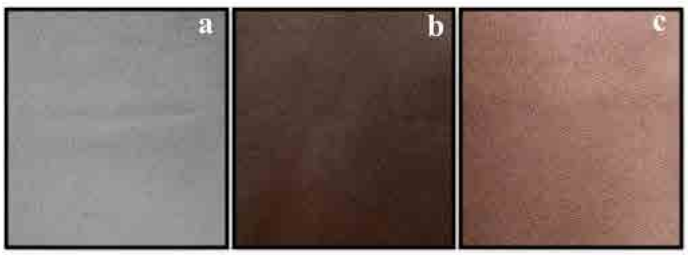

Figure 6. Surface color of the leather a) uncoated, b) coated with lignin based pigment formulation, and c) commercial brown pigment.

in the medium. The mass tone has been evaluated after applying it over the checkered card. The coated card is shown in Figure 5. The lightness factor 'L' has been measured on the white and black coated areas. It was interesting to note that the 'L' values at the white and black area are 27 and 26, respectively. Thus, it could be inferred that the separated lignin has good covering/ hiding power and can efficiently use as a pigment.

Application of Lignin Based Pigment for Leather Surface Coating

In order to inspect the applicability of separated lignin as brown pigment, the insoluble lignin treated leathers are compared with uncoated and control leathers. The experimental leathers are made with separated lignin as a brown pigment during leather finishing stage. Finishing formulation constitute of soft and medium resin binders, protein binder and soft polyurethane binder along with 40g/L separated lignin was prepared. The details about the formulation were given in the Table I. Four cross coats of the season formulation were coated onto the undyed crust leather Coated leather has been fixed with 2 cross coats of lacquer emulsion and dried. Similarly, the control leathers are made with same pigment formulations, instead of separated lignin the commercial brown pigment was used. The surface colors of the crust leather before and after coating are shown in Figure 6. The photographic images clearly show that separated lignin can uniformly coat the leather surface without any precipitation of the pigments. Especially the experimental leathers showed darker shade than control leathers due to the uniform coating. This further confirmed that the insoluble lignin has been effectively used as brown pigment for leather finishing application.

Reflectance Measurements of Pigment Coated Leather

The difference in the L, a*, b*, c and h values of the pigment coated leathers along with those of the unfinished crust leathers are evaluated and presented in Table II. It was observed that the crust leather without finishing has L value of 81±3 indicating that the leather is light in color. L value of the coated leather has been measured to be 44±2 indicating that the surface color was darker due to the pigment coating. Considering the L and h value of experimental and control leathers, there will be a minimal change in the surface color. Even the leather coated with insoluble lignin showed darker shade than control leathers. From a* and b* values it could be inferred that the coated leathers (experimental and control) has brownish hue. Higher chromaticity values again confirm the brighter surface color characteristic of experimental leathers than control and uncoated leathers. Hence it was established that the uniform coating was achieved by using separated insoluble lignin on leather surface.

Determination of Fastness Properties

Once the uniform coating was done, the coated leather has been evaluated for the fastness to rub (dry/ wet) and light. The results of the wet and dry rub fastness of the leathers are shown in Table III. The lignin based pigment coated leathers showed better fastness properties and satisfied the standards.[20-21] Similarly, the coated leather were taken for light fastness test and it was shown in Table III. The effect of ageing (40 h) on the light fastness property has also been studied. Less significant color change after exposure to artificial light divulges the good fastness properties obtained from insoluble lignin coated leather even after ageing. Overall fastness properties of experimental leather seem similar or superior to control leather.

Table II

The color coordinates of the separated lignin coated leather compared with uncoated and control leather.

S. No	Sample	L	a*	b*	c	h
1	Uncoated Leather	80.65	-4.08	-1.30	4.28	17.71
2	Experimental Leather	43.64	5.65	5.77	8.08	45.61
3	Control Leather	44.14	3.51	4.77	5.92	53.66

Table III

Rub and light fastness property of lignin based pigment coated leather.

S. No	Fastness	Grey Scale rating	
		Experimental leather	Control leather
1	Dry 512 rubs	4	3/4
2	Wet 256 rubs	3/4	3/4
3	Light fastness	4/5	4

Conclusions

The separation of insoluble lignin and using it as a brown pigment for leather finishing upholds the sustainable concepts of waste management and product development from waste black liquor. Insoluble lignin from paper and pulp industry waste black liquor was separated and characterized thoroughly to apply as pigment in leather finishing application. Comparatively, physio-chemical characteristic of the separated lignin was similar to that of standard lignin. BET and SEM characteristics confirm that the degraded phenolic product was used as pigment for leather finishing. Higher mass tone with smaller particle size confirmed that the separated lignin having good hiding power. Hence, the findings provide a clue that the developed brown lignin based pigments can be effectively used as alternative with commercially available pigments for leather surface coating. Thus, utilization of the black liquor obtained from the paper and pulp industry was identified, thereby providing an eco-benign solution for the disposal of the wastes produced by the industry.

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Abbreviations

FT-IR, Fourier transform infrared spectroscopy; TGA, Thermogravimetric analysis; DSC, Differential scanning colorimetry; BET, Brunauer Emmett Teller; SEM, Scanning Electron Microscopy; KBr, Potassium bromide; CIELAB, Color coordinates.

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