Experimental Study on Micro Surfacing using Chrome Shaving Impregnated with Modified Bitumen Emulsion

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It has been stated that about 600,000 tones of solid waste is being generated worldwide by the leather industry in which 40–50% of the hides are lost due to shavings and trimmings. Basic Trivalent Chromium (Cr (III)) sulfate is widely used as tannage material. Only 60–80% of the total Chromium (Cr) reacts with the hides and about 20–40% of the total Cr remains un-reacted in the liquor. Chrome shavings (CS) are the scrap generated during leveling of tanned skins, and mainly consisting of collagen cross linked with Cr (III). As of now, there are insufficient report and researches on the use of leather industry waste in bituminous mixes. This study focuses on the use of CS as filler in micro surfacing for pavement preservation, to overcome the burden of CS disposal. Micro surfacing is a mixture of dense – graded aggregate, polymer modified bitumen emulsion, mineral filler, and water. Therefore, in this study an experimental micro surfacing layer was laid on the heavy traffic road namely Sardar Patel Road, Chennai, Tamil Nadu, India, having more than 1500 CVPD (Type III). Another experimental section was laid on a light traffic road with less than 1500 CVPD (Type II) in the premises of Anna University, Chennai.

Keywords: Micro-surfacing, Chrome shavings, Leaching, Preservation layer, Cold-mix

Introduction

The nature of solid wastes generated from the Leather processing can be broadly classified as chemical and protein based solid waste. Processing one metric ton of raw hide generates 200 kg of final leather product, 250 kg of untanned solid waste (such as fleshing and trimming), 200 kg of tanned waste (includes shaving, trimming and splitting waste of chromium tanned leather), and 50,000 kg of waste waster1,2. Chrome shavings are small, thin pieces of chrome tanned fibrous matrix of collagen formed during the levelling operation. It accounts to 10% of the weight of raw skins/hides processed, amounting to 0.8 million ton globally3,4. Globally 30% of the leather processed in the tanneries is rejected, mainly after shaving process, in the form of protein wastes containing 3 – 5 % chromium (III)5,6. These wastes still go into land disposal5, 5,7. Due to stringent restriction on the disposal of chromium – bearing waste in many parts of the world there is a need for safe disposal of this waste. These wastes can be used for the manufacture of bonded leather, leather boards, as a filler of carboxylated butadiene – acrylonitrile rubber5,8. Considering the quantum of CS available as waste, and its reported to use as filler to form flexible material, the applicability of this waste was seriously considered for the preparation of micro surfacing pavement maintenance.

Maintenance is an essential activity for providing the required serviceability and durability of a pavement to the road user. It is established that appropriate, timely and scientific maintenance extend the service life of the pavement considerably. In construction and maintenance of roads by conventional hot mix technologies, energy inputs begin from quarrying of stones and continue till mix is finally laid and compacted. These hot mix technologies create environmental pollution. The cold-mix technologies use environment friendly materials and techniques involving use of bitumen emulsion, which can provide effective, energy efficient and long lasting maintenance solution. Microsurfacing is considered as more environment friendly alternative renewal treatment for preventive maintenance than conventional thin hot bituminous mixture9. It is applied on the entire surface of the
existing pavement, covering all the cracks and small defects and producing a skid resistant, durable and waterproofing surface. Micro-surfacing helps in preservation of pavement strength and therefore can be used both for preventive and periodic renewal treatment.

This surfacing is suggested to be useful for pavements in urban and rural areas, primary and interstate routes, residential street, highways, toll roads and runways as noise reducing surface. Sand is one of the constituent materials used in microsurfacing, as fine aggregate. Continuous sand mining for construction would lead to purposes depletion of natural resources and ecological imbalance. Therefore, an attempt has been made in this study to replace the sand in the micro – surfacing mixture with fibrous chrome shaving (CS), a solid waste generated in tannery. The CS, being fibrous in nature can serve as reinforcement material in the micro – surfacing and thus could provide more flexibility on the surface of the road. Our research is focused on the incorporation of CS in the road construction with an approach to improve the performance of CS containing bitumen mixes, as the fibrous CS is proposed to substitute the granular sand to some extent. Therefore, it is essential to have new outlook to improve the performance of such mixes by incorporation of stable fibers to extend the service life of the pavement.

Materials and methods
Chrome shavings (CS) and its characterization
CS were collected from local Pallavaram tannery and ground in advance so that the fiber would present homogeneous grain size. The surface morphology and average diameter of CS, after size reduction, was examined using S-3400 scanning electron microscope (SEM). The X-ray diffraction (XRD) pattern was recorded with Cu Kα radiation at λ= 1.54Å. The chemicals such as Carbon (C), Hydrogen (H), Nitrogen (N) and Sulphur (S) from CHNS 1108 Carlo-Erba elemental analyser. Fourier Transform Infrared Spectroscopy (FTIR), IR spectra have been measured by the spectrometer Perkin Elmer FT–IR system Spectrum X. Samples were prepared by mixing 1 mg of the sample in 200 mg of KBr. The spectral analysis was performed in the range 4000-400 cm⁻¹ with spectral resolution of 1cm⁻¹. Thermo gravimetric analysis (TGA) was used to determine the degradation temperature of raw CS, CS - impregnated in slow setting emulsion and micro surfacing emulsion designated as CS, CS/SSE and CS/PME. TGA were run on Q.50.V20.6 Thermal Gravimetric Analyzer in an atmosphere air. All the runs were carried out at a heating rate of 20°C/ min, from ambient temperature to 800°C. α-alumina was used as reference sample on platinum pans (Fig.1).

Estimation of chromium (III) and chromium (VI)
About 2 grams of CS was gently stirred for 3 h with 100 ml of 0.13 moles of dipotasium hydrogen ortho phosphate at pH 8 and filtered. 10 ml of solution was taken out and added with 10 ml of phosphate puffer and made up to 25 ml. One ml of 0.5% diphenyl carbazide was added followed by addition of 0.5 ml of ortho phosphoric acid. The solution was kept for colour development for 15 min and the absorbance was measured at 540 nm. The calculated concentration was chromium (VI). Samples were tested for the total chromium content in CS and CS encapsulated samples by using Perkin-Elmer an Analyst 700 Atomic Absorption Spectrometer. Chromium (VI) is subtracted from total chromium to get chromium (III).

Design and proportioning of micro-surfacing mix
The job mix design was performed as per IRC-SP: 81-2008, incorporation CS as fine aggregate different proportion by weight of aggregate in such a manner that it results in a uniform and homogenous blend to fit the appropriate gradation. Trail mixtures were prepared so as to get the final receipy having the setting time less than 180 sec. Different types (Type II and Type III) of micro-surfacing adopted in two locations are given in Table.1 and Table 2.

Laying of test track using CS as filler in micro-surfacing mix
An experimental road stretch with CS as partial alternate filler was used in micro-surfacing layer in the busiest road namely Sardar Patel road having more than 1500 CVPD (Type III) and another section of light traffic road having less than 1500 CVPD (Type II) in the premises of Anna University, Chennai using conventional concrete mixture. Trail sections were manually laid in 100 m² areas (Fig. 2).

Results and Discussion
Characterisation of Chrome shavings
The scanning electron microscopic image (Fig. 1), clearly indicates the fibrous morphology of CS. The physic – chemical properties of CS was determined and the values are : specific gravity 1.5; bulk density 1600 gm./cc; moisture content 15-40%; ash content
Table 1—Different types of micro-surfacing

<table>
<thead>
<tr>
<th>Application</th>
<th>Type II (Anna University)</th>
<th>Type III (Sardar Patel road)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4–6 mm, &lt;1500 CVPD</td>
<td>6–8 mm, &gt;1500 CVPD</td>
<td></td>
</tr>
<tr>
<td>Quantity of mix, Kg/m²</td>
<td>10.8</td>
<td>16.3</td>
</tr>
<tr>
<td>Residual binder (% by weight of dry aggregate)</td>
<td>10.5</td>
<td>10.5</td>
</tr>
<tr>
<td>Sieve size, mm</td>
<td>Specified gradation limits</td>
<td></td>
</tr>
<tr>
<td>9.5</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>6.3</td>
<td>100</td>
<td>90–100</td>
</tr>
<tr>
<td>4.75</td>
<td>90–100</td>
<td>70–90</td>
</tr>
<tr>
<td>2.36</td>
<td>65–90</td>
<td>45–70</td>
</tr>
<tr>
<td>1.18</td>
<td>45–70</td>
<td>28–50</td>
</tr>
<tr>
<td>0.600</td>
<td>30–50</td>
<td>19–34</td>
</tr>
<tr>
<td>0.300</td>
<td>18–30</td>
<td>12–25</td>
</tr>
<tr>
<td>0.150</td>
<td>10–21</td>
<td>7–18</td>
</tr>
<tr>
<td>0.075</td>
<td>5–15</td>
<td>5–15</td>
</tr>
</tbody>
</table>

13%; average fibre length 1100 – 1300µm; average fibre diameter 170 µm; pH 3.0 -4.1% and temperature resistance up to 200°C. The elemental analysis showed that CS having C - 37.3%; H - 6.54%; N - 15.6% and S - 14.53%. The diffractogram revealed the presence of calcium chromate (CaCrO₄) and calcite (CaCO₃). The peak noted at 2θ = 26 can be attributed to CaCrO₄·H₂O. The IR spectrums obtained for CS shows the presence of following functional groups i.e., Hydrogen bonded – alcohols, phenols (O-H, 3300 cm⁻¹), alkenes (C=C, 1638 cm⁻¹), nitro compounds (NO₂, 1544 cm⁻¹), alkenes (C-H, 1477 cm⁻¹) and amines (C-N, 1237 cm⁻¹). The thermo gram of either CS alone or CS impregnated – cationic slow setting emulsion and - SBR modified emulsion divulge the fact that the Chrome-tanned biological fibre is degraded in a single stage, when it is heated between the ambient temperature (30°C) and 800°C. The pyrolytic pattern also reveals that the chemically stabilized collagen fibre (chrome tanned leather shaving) is thermally stable up to 250°C after which it started losing weight. Thermo
Table 2—Mix Design of Micro surfacing for 100 m$^2$ area

<table>
<thead>
<tr>
<th>Material</th>
<th>Micro surfacing (Anna University Chennai)</th>
<th>Micro surfacing (Sardar Patel Road, Chennai)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aggregate 6.3 mm sieve size</td>
<td>200</td>
<td>200</td>
</tr>
<tr>
<td>(Sand for Slurry seal), kg</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Portland cement, kg</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Chrome shaving, kg</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>Water, litre</td>
<td>10</td>
<td>12</td>
</tr>
<tr>
<td>Polymer modified emulsion, kg</td>
<td>50</td>
<td>50</td>
</tr>
</tbody>
</table>

Leaching property of chromium in CS and CS impregnated sample

The CS containing sample was studied for its leaching property by TCLP method. It was found that the CS and encapsulated CS sample showed a maximum of only 0.3 ppm of leachate Cr, which is far less value compared to the permissible limit 5 ppm as per Environmental Protection Agency (EPA) test method D007$^{20,21}$. The leachate of encapsulated samples was further analyzed to find out the other heavy metals present in the samples. It was observed that it had Cu, Pb and Zn to a level of 0.02, 0.23 and 0.26 ppm respectively. There is no evidence of colour changing in the diphenyl carbazide absorption at 540 nm. It is quite evident that the IR band (Fig. 1) absence near 875.57 and 712 cm$^{-1}$ confirms the prevention of Cr (III) to Cr (VI) conversation in the CS and CS encapsulated with polymer modified emulsion$^{22}$.

Laying of test track using CS as filler in micro-surfacing mix

Two experimental section were laid on a structurally sound roads on Sardar Patel road (> 1500 CVPD) and in Anna University Campus (< 1500 CVPD) in the year 2010. The experimental sections were laid using conventional concrete mixer with the help of skilled labour (Fig. 2). These mixtures were laid manually without using micro-surfacing machine. The CS powder mixed into the fine aggregate does not make any lumps during preparation of slurry. The SBR modified micro-surfacing emulsion was compatible with the mixture of fine aggregate, CS and cement. Thus, this combination could be an alternate method of laying micro-surfacing where there is no facility of micro-surfacing machine. In both the cases about 5% CS was used as filler in the slurry. The trial section was very prone to oxidation, as a result, the presence of oxygen promotes chemical reactions to takes place at higher temperature, generating functional groups such as -C=O or -COOR on the main polymer chain. The bond energy of C=O is higher than that of the C-C or C-H bond; the (bond energy of C=O, C-H and C-C are 724, 410, and 335 kJ/mol, respectively$^{17}$. In addition to that the unsaturation brought out in the molecular chain may be promoting the cross-linking reaction$^{18}$. The cross-links are formed mainly between C-C and C-O. The cross-links thus formed provide the polymer an enhanced rigidity and imparts a higher thermal stability to cross-linked SBR$^{19}$. 

Gravimetrically, after an initial weight loss of approximately 7% up to 200°C, a major and sudden weight loss of about 50% was noticed between 200°C-465°C, thereafter the pyrolysis proceeds in a slow pace where another 15% loss was observed on thermal decomposition pattern after the till end. On the other hand, thermal decomposition pattern of the CS-impregnated polymeric material varies depending upon the chemical nature of its polymers. Accordingly, the degradation takes place in two-stages: the first stage of degradation of SBR are due to the volatile products originating from the butadiene part and the second stage decomposition that occurs in the temperature range of about 292-497°C contribute to a weight loss 10.48%. The degradation involves the scission of the main chain macromolecular chain. The double bonds presents in SBR become saturated and -CH$_2$-CH$_2$- segments are generated. These -CH$_2$-CH$_2$- segments are relatively stable to heat due to the higher bonding energy of the C-C single bond$^{15}$. The rate of pyrolysis of SBR, observed between 292-497 °C is higher in the presence of air. However, a decreased rate of thermal degradation of SBR in the presence of nitrogen was observed$^{16}$. The double bonds in the SBR latex are

Fig. 2—Microsurfacing using chrome shavings as filler after one year of construction laid at Sardar Patel Road, Chennai.
blocked for traffic for a period of three hours for breaking of emulsion, after three hours the traffic was allowed. With the movement of traffic, the slurry was self heeled and compacted. The section was continuously monitored for its performance for a period of three years.

Conclusion
Based on the observation from various experiments conducted using CS as filler, the bitumen encapsulated mix was found to be stable in water. Chrome shavings as fine aggregate in micro-surfacing at concentration of 2-5% (w/v) can be successfully used. The mix can be uniformly laid by using wooden confinement according to the thickness prescribed in ISSA. The cold bitumen emulsion used in this study was polymeric in nature and fulfilled the physical requirement as per IS: 8887. The surfaces were monitored for two years on pre and post monsoon as well summer season. It was found that these surfacing would serve as pavement preservation layer or alternate routine maintenance treatment of urban roads. The design and construction of micro-surfacing mix was carried with the available resources at Central Leather Research Institute, Chennai, India. Taking the thermogram values into account, a detailed laboratory trial will be carried out to modify the conventional bitumen using the CS as modifier. The CS is likely to be converted into a brittle gelatinous material at high temperature when used with hot bitumen.

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References