Production of Asphaltene Binders from Solid Waste Generated in Leather Industry

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ABSTRACT

India is one of the major leather producers and nearly 0.75 million tons of raw hides/skins are processed annually. Conversion of 1 ton of rawhide/skin into leather generates nearly 200 – 300 Kgs. of solid waste and rest of the material is converted into leather. Some of the solid wastes such as raw hide/skin trimmings, fleshings, chrome shavings, leather trimmings find uses in other industries, however, waste like buffing dust do not find any use. As they are fine particles and also contain chromium, current practice of dumping in vacant site causes severe health and environmental problems. The obnoxious gases such as oxides of sulphur, ammonia and other volatile organic compounds are emitted from tannery buffing dust during the thermal decomposition. In the present work, an attempt has been made to make leather waste into modified bitumen a pavement material through pyrolysis followed by solidification/stabilization process. The pyrolysed tannery buffing dust was characterized by SEM, FTIR, TGA, and CHNS analyzer. The pyrolysed TBD was effectively solidified/stabilized using aged bitumen. Pyrolysed solid tannery waste is made into modified bitumen and analysed for its rheological characteristics. The leachability of the stabilization of Cr (III) in the solidified matrix was confirmed through TCLP method. Thus, this study illustrates the recycling of buffing dust, a problematic waste in leather making to a societally useful material for road construction.

***Key words**:* buffing dust – pyrolysis – Chromium (III) – solidified blocks – Modified bitumen

I INTRODUCTION

Now days, tanneries are looking for new ideas and initiatives pushing sustainability to a higher innovative level. It is well known that production of leather is one of the major producers of hazardous solid wastes, with high potential impact to the environment. The production of chromium-containing solid waste in tanneries has been recognized as a problem for many years, and increasing pressure from environmental authorities has demanded a solution of such a problem (Gammoun, 2007). Only 20% of wet salted hides/skins could be converted into commercial leather, and 25% mass becomes chromium-containing leather waste (CCLW), and the remnant becomes non-tanned waste or is lost in wastewater as fat, soluble protein and solid suspended pollutants. Shavings, trimmings, buffing dust and splits from the chromium tanning of hides and skins have been disposed of in landfills. Increasing local legislations on waste disposal, unavailability of land, high operation cost incurred in conventional treatment systems like land filling and incineration have stimulated the search for better, cost effective and eco-friendly treatment. Among the pollution abatement strategies, source reduction is good; however, process modifications could not be adapted. Next best available option observed is recycling and reusing of waste materials (Brown, Cabeza, Silveria, Mu, Kamaludeen, Rivela, and Saravanabhavan, 1996a, 1999b, 2002c, 2003d, 2003e, 2004f, 2004g).

Pyrolysis, of wastes is one of the best methods that could render reusing of waste as it can convert wastes into gas, liquid, and solid fractions with different end applications. Also, the energetic efficiency in pyrolysis is lower than that in combustion, makes the process cost effective too. The gas that produced during pyrolysis can be re-used as fuel and the oil can be used as a raw material for chemicals. The carbonaceous residue can be burnt as fuel or safely disposed fixed on the carbonaceous matrix [Cassano, Imai, Petruzelli, Sivaparvathi, Sivaparvathi and Yilmaz, 1997a, 1991b, 1995c, 1986d, 1986e, 2007f).

Solidification/stabilization is another technique for disposal of solid waste containing heavy metals as they can protect the environment from contamination. Stabilization involves mixing of wastes with binding agents like cement, asphalt, fly ash, clay etc. Many research works have been performed using this technique for recycle of leather wastes such as tannery sludge with clay (Basegio, 2002) tannery waste with ceramics (Abreu, 2009), incinerated chrome shavings with alumina[Abreu and Basegio 2009a, 2006b), stabilizing of tannery waste with building materials(Xu, 2009), solidification with cement and aggregates(Abtahi, 2010).

In this paper the carbonaceous matrix of the tannery solid waste containing the chromium metal was pyrolysed to produce Micro Fibre Carbon (MFC) and further utilization of MFC for making modified bitumen. The purview of the current research is to study about the behaviour of chromium after a pyrolytic process and the stabilization process. Chromium is bounded in the pyrolytic residual ash compared to the TSW on both oxidation states Chromium (III) and Chromium (VI).

II MATERIALS AND METHODS

(a) Collection and characterisation of TSW, MFC and Modified Bitumen

TSW used in the study was collected from Blue Diamond leather manufacture industry in Chennai, Tamil Nadu. The TSW and MFC were characterized for moisture content, ash content and Chromium (III) and chromium (VI) according to the DIN protocol, Thermo-gravimetric analysis such as (TGA), elemental analysis like carbon, hydrogen, nitrogen and sulphur (CHNS), studies were carried out to determine the oxidation state of chromium in the TSW and MFC, thermal stability, elemental composition in the TSW and MFC respectively. SEM analysis were carried out to determine the morphology of MFC and Modified Bitumen, Fourier transform infrared (FTIR) studies were carried out to determine the functional groups in the MFC.

III INSTRUMENTAL ANALYSIS

TGA was carried out to determine the weight loss with respect to temperature in order to fix the heating segment pattern of incineration. The dried samples were analyzed under nitrogen atmosphere using Q50 TA instruments. The samples were heated in a platinum pan from 0 to 800°C at the rate of 5°C/min. The elemental CHNS content of the TSW, MFC was determined using CHNS vario micro CHNSO15091002 analyzers. SEM analysis of MFC and modified bituminous mixture was determined using Hitachi S-3500N scanning electron microscope. FTIR of MFC can be determined by Perkin Elmer spectrum two instruments.

(a) Estimation of chromium (III) and chromium (VI)

About two grams of the TSW sample was gently stirred for 3 h with 100 ml of 0.13 moles of dipotassium hydrogen ortho phosphate at pH 8 and filtered. Out of it, 10 ml of the solution was added with 2 ml of 2N sulphuric acid and made up to 25 ml. 2 ml of 0.5% diphenyl carbazide was added followed by the 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). Total chromium was estimated using the above method after digesting the samples using acid mixtures (10 ml HNO_3: 10 ml H_2SO_4: 10 ml HClO4) followed by the oxidation using potassium permanganate and sodium azide. Chromium (VI) is subtracted from total chromium to get chromium (III).

(b) Moisture content

The moisture content was calculated by Equation (1). Initially, 2g of sample was taken in the silica crucible and placed in the air oven at 110°C after 1hour, cools the sample and taken the final weight of the sample.

$$\text{Moisture content } (\%) = (\text{Initial weight} - \text{final weight})/(\text{initial weight})\ \text{X } 100 \qquad (1)$$

(c) Ash Content

The Ash content was calculated by Equation (2). Initially, 2g of sample was taken in the silica crucible and placed in the furnace at 550°C after 1hour cools the sample and taken the final weight of the sample.

$$\text{Ash content } (\%) = (\text{Initial weight} - \text{final weight})/(\text{initial weight})\ \text{X } 100 \qquad (2)$$

IV PREPARATION OF MICRO FIBROUS CARBON (MFC)

The pyrolysis of a TSW in the O_2 atmosphere has been carried out in a stainless steel (316 grades) vertical retort of weight 13 kg, which was placed inside an electrical furnace. The outer jacket of the lid of the pyrolysis vessel was fitted with pipe, it has 7cm thickness in order to prevent condensation of volatile organic compounds back into pyrolysed vessel, which increases energy recovery efficiency and prevents the heat dissipation from the reactor. The Condensed organic compounds are collected in the condenser. The flue gas from the incinerator was scrubbed in a scrubber. The scrubber is a PVC column of height 1.5 and 0.175m diameter to remove acidic vapours using alkaline water. Water required for scrubbing the flue gas was provided through a pump of capacity 0.5 HP. Provisions were made for characterizing the scrubbing solution used in the scrubber. The MFC collected from the Stainless steel vessel.

V SOLIDIFICATION AND STABILIZATION OF MFC

(a) Preparation of bituminous mixture

The residual ash (MFC) was collected from the furnace after pyrolysis of TSW was powdered and quantified. Aged bitumen (HRRC, Tamilnadu) was used as a binder. Asphalt mixer horizontal AIM 575was used to prepare the Asphalt mixture blocks.

This machine is used for laboratory mixing of bituminous materials to prepare the specimens to be used for various asphalt tests. The machine mainly consists of a main frame, variable speed mixer, elevating system, heating pot, electrical control box. About 100g of aged bitumen and various amount of residual ash (1 to 15g) was mixed for making of modified bitumen. It was prepare to mix in the heating pot with the variable speed mixer. The mixing portion taken from the heating pot and transfer to aluminium sample container and AIM 512-1 universal Penetrometer was used to determine the penetration value of modified bitumen.

VI RHEOLOGICAL CHARACTER OF MODIFIED BITUMEN

Penetration Test of modified bituminous mixture was determined to using AIM 512-1 model instrument. The bituminous mixture was taken in the aluminium container and the test is carried out in the room temperature. Softening Point Test of the modified bituminous mixture carried out by AIM 561-1 model instrument, this ring ball method give characteristic nature of the modified bitumen. AIM 532 model instrument is used for determine the viscosity of the modified bitumen.

VII LEACHABILITY TEST

The leachability of the metals from the solidified samples of pyrolysed TSW blocks were determined by Toxicity Characterization of Leachate Procedure test (TCLP). TCLP is designed to determine the mobility of both organic and inorganic analytes present in liquid, solid and multiphase wastes. It is usually used to determine EP toxicity of a hazardous waste. The bituminous mixture of weight 20 g was placed in a TCLP cylinder with 100 ml of extraction fluid (5.7 ml of glacial acetic acid in 500 ml of water and then adjust to pH 4.95). The contents were agitated in a TCLP rotator agitator at 30 rpm for 18 h and the liquid phase was separated from the solid phase by filtration through a 0.6–0.8 μm borosilicate glass fibre under pressure of 50 psi (340 KPa). The liquid phase was analyzed for chromium (III) and chromium (VI) ion to determine metal fixation efficiency.

VIII RESULTS AND DISCUSSION

(a) Characteristics of buffing dust

The moisture content, ash content, Chromium (III) and chromium (VI) of the TSW were 4.51%, 87.51%, 0.73 mg/g, 65.48μg/ml respectively.

(b) Elemental analysis

The elemental composition of the TSW was Carbon 52.7274%, Hydrogen 2.8038%, Nitrogen 8.9150%, and Sulphur 2.8902% (67.3364%). The elemental analysis suggests that 67.3364% of the organic matter in the TSW and remaining 32.6636% were inorganic components like metal salts.

(c) TGA analysis

TGA of TSW (Fig. 1) shows that the weight loss at 94.1°C is due to elimination of moisture as well as organic volatile compounds. The organic compounds of TSW such as tannin, synthetic tannin, protein and fatty substances are hydrophilic in nature and thus the water molecules are held in the bound form and, ammonia, methane compounds are coming in the TGA before turning 100°C because these salts and solvents are used in the leather processing. TGA records a weight loss in the temperature ranges from 240.3 to 576.5°C, which can be attributed to the decomposition of organic compounds in the TSW into intermediate compounds. The intermediate compounds were volatilized off that left behind the ash content in the temperature range from 679.4 to 790.6° C. The ash contains only 5% of inorganic compounds like metals and metal salts. The remaining things are decomposed.

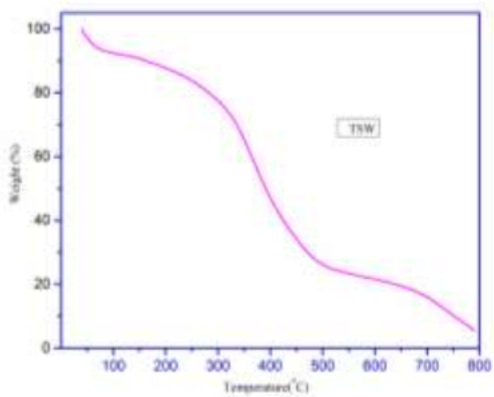

Fig .1 TGA analysis of TSW

IX CHARACTERIZATION OF MICRO FIBROUS CARBON (MFC)

(a) Characteristics of MFC

The moisture, ash, Chromium (III) and Chromium (VI) contents of the MFC were observed to be 2.69%, 74.42%, 0.81 mg/g and 5.50 μg/g respectively.

(b) Elemental analysis

The elemental composition of the MFC was Carbon 49.4282%, Hydrogen 1.2041%, Nitrogen 3.1769%, and Sulphur 1.7624% (55.5716%). The elemental analysis suggests that the MFC contains inorganic components because after pyrolysis most of the organic matters are decomposed and converted to carbon. The carbon contains mainly oxygen and metal so elemental analysis give the idea about the composition of element in the carbon it's further conformed by EDX spectrum.

(c) TGA of MFC

The fig.2 shows the TGA analysis of MFC. Initially the weight loss at 65°C show the moisture present in the MFC and huge weight loss (72%)in the range like 291-347 °C shows the carbons are easily converted to ash because all organic parts pyrolysed to convert inorganic carbon and remaining inorganic compounds comes at residue at 790° C.

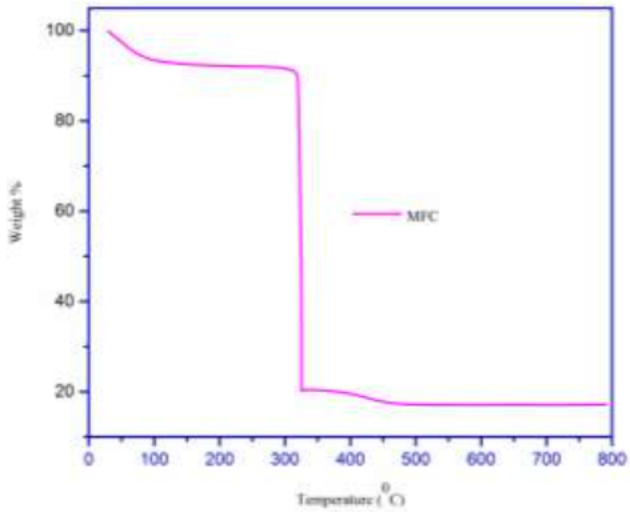

Fig .2 TGA analysis of MFC

(d) FTIR of MFC

The fig .3 shows the FTIR spectrum of MFC. It has a strong and broad band at 3500-3000cm^{-1} for the atmospheric water present in the MFC and band at 1580 and 1145cm^{-1} aromatic and C-O stretching frequency of MFC due to the aromatic group in condensed liquid may comes in the solid part and carbon adsorbed some amount of oxygen in this surface. The peak at 547 and 472cm^{-1} is due to the presence of metal oxide band (chromium oxide).

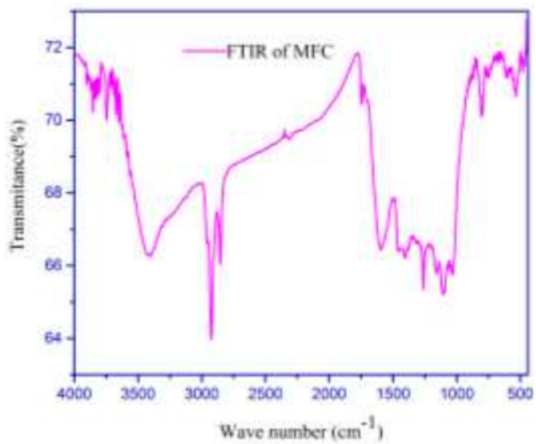

Fig .3 FTIR analysis of MFC

(e) SEM with EDX analysis of MFC

Fig. 4 showed SEM photographs of MFC. MFC prepared through the pyrolysis of TSW, the TSW pyrolysis to 30-800°C at varies time segment produce micro fibres in the resultant residual ash. The shrinkage by the pyrolysis may make the size of residual ash smaller from the TSW in the order of several tens micrometers. The temperature is the most important factor which determines the size and shape of the MFC growth after pyrolysis. The one more factor is presence of metal or metal salts determines the fibrous structure of the residual ash (MFC).The MFC rope (fig. 4(b)) can be easily distinguished and the metal particles are dispersed in the product it is clearly show in the fig. 4(a). The average diameter of the MFC can be determined and the diameter is 129 nm. EDX spectral analysis (table.1 and fig. 5 intensity of metal peaks) reveals that the MFC contains approximately 78.04 Wt% carbon, 0.59 Wt% Chromium, 19.91Wt% oxygen and of, 0.68 Wt% chlorine, 0.78Wt% silicon. The organic compounds in the tannery solid waste are decomposed after pyrolysis and remaining part contains mostly inorganic compound like carbon, metal and metal salts.

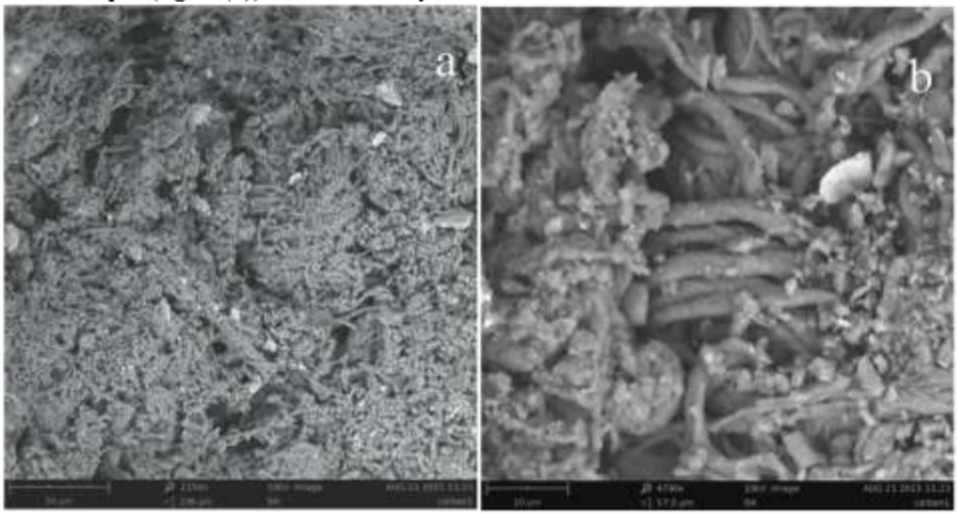

Fig .4 SEM analysis of MFC

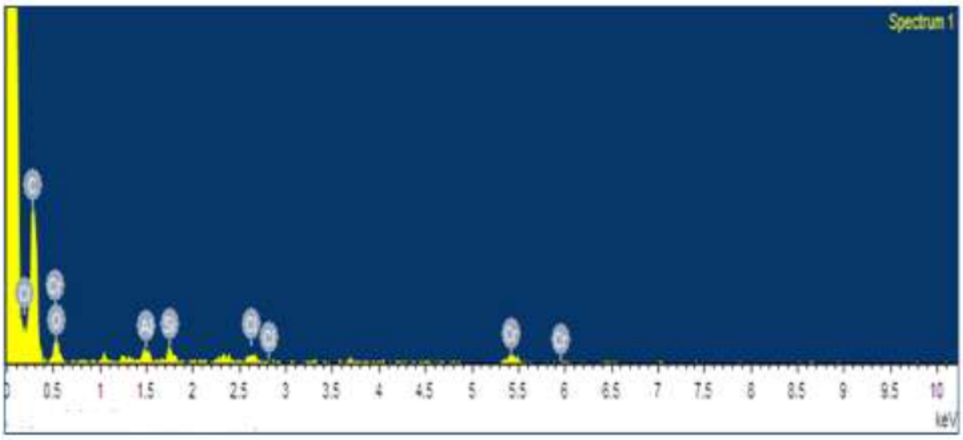

Fig .5 EDX spectrum of MFC

Table 1
EDX spectral data of MFC

Element	Approximate Concentration	Intensity concentration	Weight%	Weight% Sigma	Atomic%
C K	16.86	0.9661	70.33	3.96	78.04
O K	2.11	0.3542	23.90	4.00	19.91
Si K	0.38	0.9304	1.65	0.34	0.78
Cl K	0.37	0.8285	1.81	0.36	0.68
Cr K	0.45	0.7911	2.30	0.60	0.59

X CHARACTERIZATION OF MODIFIED BITUMEN

(a) SEM analysis of modified bitumen

The SEM image of modified bitumen shows in the fig. 6. The both the picture(c and d) tells about the microfiber carbon material bind with the bituminous material due to the fiber structure are show clearly in the second picture at the same time it is show block in colour and some of the cubical particle show in the picture due to the presence of metal in the MFC it also bind with the heteroatom present in the bitumen and MFC penetrate the bitumen due to the presence of layer in the bitumen.

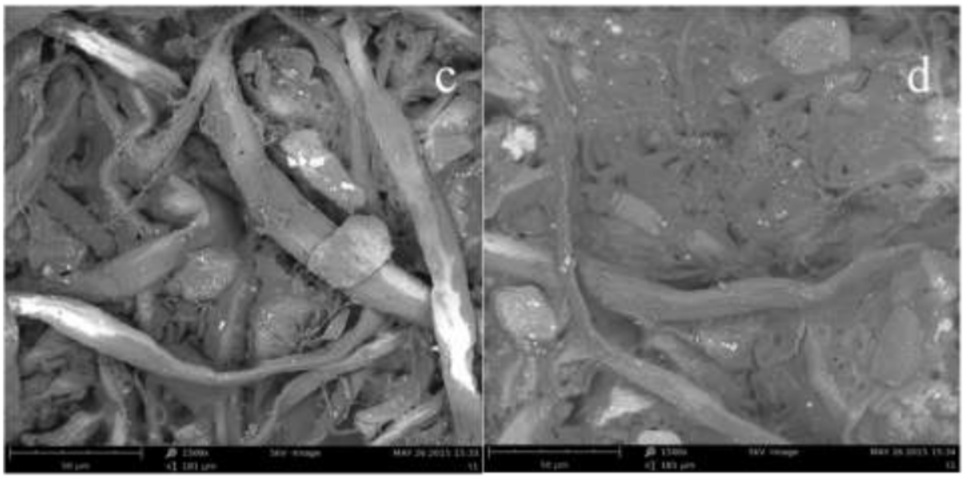

Fig .6 SEM analysis of modified bitumen

(b) Rheological test for modified bitumen

Table 2
Rheological tests for Modified Bitumen

Modified bitumen samples	Penetration values (dmm)	Softening Point (Temperature when ball touches the bottom, ^{O}C)	Viscosity (220 ^{o}C, time taken to flow 50cc of the binder)
Control	31	58	36
5% MFC	27	67	57
10% MFC	23	86	62
15% MFC	21	100	67

(c) Penetration Test for Modified Bitumen

Fig .7(a) and table. 2 show the penetration test for the modified bitumen. The aged bitumen is show the penetration around 31dmm but with the addition of MFC (1to 15g) the penetration value should be decreased because the addition MFC can binding with the aged bitumen and brittleness of the aged bitumen is changed.

(d) Softening Point for Modified Bitumen

The softening point of the modified bitumen is increase compare with control, the addition of inorganic matrix can change heating resistance of the bitumen. So the compound is thermally stable compare with control. Fig 7(b) and table. 2 results indicate the modified bitumen can change the character of the aged bitumen.

(e) Viscosity of Modified Bitumen

Viscosity of modified bitumen is decreasing with time. The modification of the aged bitumen strongly binds with the MFC, its decrease the viscosity of the control at the same time the brittle nature of the control should be changed. In the fig. 7(c) and table. 2 clearly tell this modification decrease the viscosity of the modified bitumen gradually with addition of MFC.

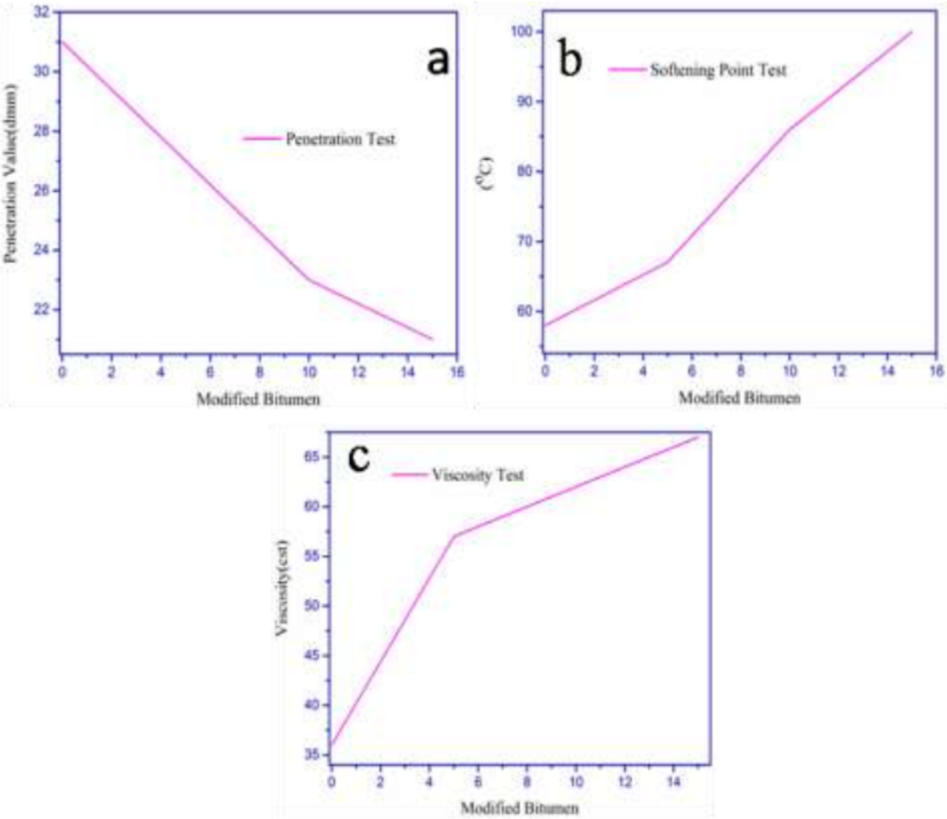

Fig. 7 Rheological character of modified bitumen

XI CONCLUSION

Successful pyrolysis of tannery buffing dust was done and micro fibrous carbon of particle size in the range 50 nm – 70 nm was prepared. The behavior of chromium under pyrolytic process was studied. Solidification and stabilization of chromium as modified bitumen was carried out. The rheological test results shows that the penetration decreases, softening point increases and the viscosity also decreases. The TCLP analysis shows there is no leaching of chromium (III) and chromium (VI) after solidification and stabilization.

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