

PREPARATION AND CHARACTERIZATION OF NANO-REINFORCED LEATHER WASTE FIBER-EPOXY NANO COMPOSITE

by

VENKATASUBRAMANIAN SIVAKUMAR,* T. R. SWATHI, RESMI MOHAN AND ASIT BARAN MANDAL

Chemical Engineering Division, CSIR-Central Leather Research Institute

ADYAR, CHENNAI – 600 020, INDIA

ABSTRACT

Significant quantities of leather waste fibers are generated from the leather industry. Confinement and utilization of leather waste fibers by converting them in to useful materials such as nano-composites is desirable. Earlier studies on making composites from leather waste fibers suffer from strength properties for different applications. In this paper, preparation and characterization of nano composite from leather fiber-epoxy polymer reinforced with nano TiO_2 has been studied and reported for the first time. Physical testing of these nano composites shows better strength and other properties for improved performance as versatile material. TGA and DSC studies revealed better thermal stability (up to 330°C) for these nano composites. FTIR analysis shows possible chemical interaction between epoxy polymer and leather fiber. Better solvent resistant property was also noticed for the nano-composites prepared. SEM analysis indicates uniform nano-composite structure and distribution of nano TiO_2 in the matrix. The present approach not only offers a solution to the disposal problem regarding leather solid wastes like buffing dusts, but also offers a versatile nano composite material.

INTRODUCTION

In tanning industry, raw skins/hides are converted into leather by means of sequential chemical and mechanical operations generating large amount of solid wastes. These solid wastes can be broadly classified into un-tanned collagen, tanned collagen (leather) and non-protein wastes as show in Figure 1. Among the tanned collagen wastes, chrome leather wastes form major part, which includes trimmings, shavings and buffing dusts and pose major environmental concern in disposal. Out of 1000 kg of raw hide, nearly 745 kg is generated as solid wastes in leather processing.¹ Only 255 kg of the raw material is converted into usable leather including leather splits. Process technology for making useful split leathers is available elsewhere.² Typical tannery solid waste

generated in tannery are: 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.^{3–5} Buffing dust is a micro fined solid particulate impregnated with chromium, synthetic fat, oil, tanning agents and dye chemicals. CBD contains chromium, which upon leaching causes environmental pollution due to leather waste particulates.⁶ Therefore; there is a need for suitable methodology for utilizing leather solid waste fibers such as buffing dusts for making nano-composites.



Figure. 1. Scope of the present work: Different solid wastes generated in leather processing and their possible utilization.

*Corresponding author e-mail: vsivalclri@gmail.com

Manuscript received March 14, 2015, accepted for publication August 7, 2015.

Nano-composites Using Leather Waste Fibers

Recycling of chrome-tanned leather waste in acrylonitrile butadiene rubber⁷ and studies on polyamide-leather wastes polymer composites⁸ were reported earlier. The use of buffing dust waste as a resource for making leather like sheets has been studied earlier.⁹ Confinement of leather waste fibers by converting them in to useful products such as composites is shown in Figure 1. Currently available composites from leather fiber wastes lack strength properties required for various applications.¹⁰ Nano-materials are capable of providing reinforcement to conventional polymer based composites.¹¹ The present paper relates to unique process for making novel reinforced nano-composite from leather waste fibers and epoxy polymer using nano TiO₂, as reported for the first time. They are expected to provide adequate physical and other properties as a versatile material for variety of applications such as light weight construction materials, automotive nano-composite, leather products foot wear components and electrical switches etc.

Epoxy polymers find wide applications in terms of high modulus and strength, and good performance at elevated temperatures; it has been chosen as the polymer matrix in this work for making nano-composites. They possess good adhesive property for binding leather waste fiber particulates in order to produce suitable composite material. They have good chemical and environmental resistance and insulation properties. They show low shrinkage on curing with excellent moisture resistance, excellent electrical, thermal resistance, and impact resistant.

Literature Survey on Composites from Leather Wastes

Preparation of nano-composite adsorbent material from Al-Zr tanning waste was reported.¹² Reconstituted leather was prepared earlier as a product from fibrillated leather fibers and

copolymer binding agent.¹³ Nano-composite was prepared with a functional contact with the substrate and silane material of the R_x-Si-A_{4-x}.¹⁴ Composite comprising of leather, non-leather fibers, a binding agent and other materials; the substrate and or the composite can be chemically or mechanically embossed.¹⁵ A study has been made on the preparation and characterization of leather particulate-polymer composites (LPPCs) from solid wastes (chrome shavings/buffing dusts) generated during leather manufacturing processes¹⁰ utilizing rubber based polymers materials. Acrylonitrile-Butadiene-Styrene (ABS) as the matrix and leather buffing powder as reinforcing filler to prepare a particulate reinforced composite has been studied.¹⁶ Studies on the preparation and characterization of poly (vinyl butyral)-leather fiber composites were also reported.¹⁷ Leather-epoxy interpenetrating polymer networks (IPNs) were synthesized earlier.¹⁸ However, there are some drawbacks of the earlier reported work as explained below.

Drawbacks of Earlier Processes/products

Based on the reported literature available, the following points highlights to establish the technical problem(s) and some of the drawbacks which needs to be solved from the earlier products/processes:

- Earlier studies related only to composites not incorporating nano materials which could able to reinforce and improve, otherwise the inferior composite strength utilizing materials such as buffing dust or
- Nano-composites formed earlier are other than versatile epoxy polymer with excellent adhesion and other properties.

TABLE I
Various experimental compositions of nano-composites prepared utilizing buffing dust leather waste fibers.

Material Code	Epoxy polymer (g)	Leather Fiber Waste (g)	Total Polymer/ Leather fiber, wt %	Curing
C1	10	1	10	Heated in oven at 70°C For 3 h. (HT)
C2	10	1	10	AT
C3	10	0.5	5	HT
C5	10	0	-	HT
C6	10	1 + 0.05 Filler A (Nano TiO ₂)	10	HT
C7	10	1+ 0.05 Filler B (Anatase TiO ₂)	10	HT

Objectives of the Present Work

The main objective of the present paper is about making leather fiber epoxy nano-composite material in order to provide requisite strength properties such as tensile strength, hardness etc. and improved chemical properties for various applications. Further, the process for the preparation of the nano-composite and its characterization were explained.

EXPERIMENTAL

Materials

Polymer matrix was prepared by mixing standard epoxy resin and hardener of Huntsman Advanced Materials (India) Pvt. Ltd. Titanium Di oxide (mixture of Rutile and Anatase) as a nano powder, < 100 nm particle size with CAS No. 13463-67-7 was obtained from Sigma Aldrich. Nano powder of Titanium-di-oxide with 21 nm particle size was also obtained from Sigma Aldrich. Leather waste buffing dust with particle size of the leather fiber in the range of (1–5 mm) was obtained from the CLRI tannery division.

Preparation of Nano-composite from Buffing Dust

Various compositions for the preparation of nano-composites from Buffing dust leather fiber are given in Table I. The product of leather fiber epoxy nano-composite and composition for preparing the same has been patented¹⁹ by CSIR-CLRI.

Typically, i) 10 g of epoxy resin and hardener system was taken to make 10 g epoxy polymer ii) Buffing dust leather fiber (< 5 mm size) and iii) Nano TiO₂ powder 5 wt.% (%w/w based on leather waste fiber wt.) were taken and mixed well using a mortar and pestle. Then the nano-composite mixture so prepared was cured in a hot air oven at 70°C for 3 hours. Then 6x6 cm nano-composite sheets were cut from the cured material. Experimental variations using two types of nano powder, amount of buffing dust (Table I) were performed and the cured nano-composite sheet was used for further testing and characterization.



Figure 2a. Sample C6



Figure 2b. Sample C7

Figure. 2. Photograph of the nano composites prepared using epoxy-leather waste fiber (Figure 2a. Sample C6 using Nano TiO₂; Figure 2b. Sample C6 using Anatase nano TiO₂).

Testing of Nano-composites from Buffing Dust

Nano-composites were tested for various physical properties such as hardness and tensile strength, which are important for different applications.

Stability of the composites against various solvents has been analyzed by treating with different solvents. Chemical composition of the composites was analyzed using FT-IR analysis. Thermal properties were tested using thermo gravimetric analysis (TGA) and differential scanning calorimeter (DSC) analysis.

Scanning Electron Microscopic (SEM) Analysis

Microstructure of cross section of nano composite obtained has been studied using SEM analysis. Nano composites were cut into uniform sizes and then gold coated using *Edwards sputtering device*. Analysis was performed using *Leica Cambridge Stereoscan 440 Scanning Electron Microscope*. SEM analysis of the nano composites (using Anatase and Nano TiO₂) has been made.

RESULTS AND DISCUSSIONS

Nano-composite Utilizing Leather Waste Fiber and Epoxy

Photographic images of nano-composites prepared from buffing dust leather fiber are shown in Figure 2a and 2b. The photographs show nano-composites utilizing leather waste fibers form good versatile material, which could be useful in various applications.

Hardness Test

The samples were tested for Shore D hardness by indentation. In general Shore D hardness is performed only for plastic like materials. The blank sample containing no leather waste fiber

TABLE II
SHORE D hardness test results
of various nano-composites
prepared prepared utilizing
buffing dust leather waste fibers.

Material code	Shore D Hardness (Range)
C1	62 – 72
C3	44 – 62
C5	52 – 58
C7	64 – 76

TABLE III
Strength properties of various nano-composites prepared prepared utilizing buffing dust leather waste fibers.

Material Code	Maximum Load (N)	Tensile Strength (M Pa)	Elongation at Break (%)	Extension at maximum load (mm)	Thickness (mm)	Length (mm)
C1	275	14.86	7.78	2.33	1.85	30
C3	106.03	6.63	16.11	4.83	1.60	30
C5	97.43	4.43	9.44	2.83	2.20	30
C6	339.32	15.08	6.11	1.83	2.25	30
C7	261.09	18.92	10.00	3.00	1.38	30

and only pure resin have also been tested and compared with other samples. Total of five readings were taken at different points and are averaged. From the Table II it has been found that the sample (C7) with nano TiO₂ (21 nm) showed high hardness number followed by other composites. The reason could be due to nano filler forming a stable reinforcement of epoxy polymer. The results also show the hardness increased with the increase in the increasing percentage of the leather waste in the polymer matrix as compared to polymer alone.

Tensile Strength

The test specimen's with 1x5-cm were cut from cured samples for tensile strength analysis. Tensile strength was measured using Instron universal testing machine. The results for the tensile tests for (nano) composites with leather particulates are shown in Table III.

The results show that the tensile strength values for the composites are significantly higher than those found for neat polymer. However, the tensile strength tends to increase slightly when the amount of leather waste in the composites increases. This behavior may be related to the good interfacial adhesion observed by the continuity of the leather fiber agglomerates with the polymer forming composite matrix. The system exhibits good interfacial adhesion of the polymer with the leather fiber and transmitted the stress of one fiber layer to another. Nano-composites (C6 and C7) prepared have better strength properties due to enhanced reinforcement of the matrix with nano particles.

Thermo Gravimetric Analysis (TGA)

TGA analysis was performed using Du Pont TGA 2950 (Delaware, US). The thermal stability was evaluated for Leather particulate – polymer composite system using TGA

analysis as shown in Figure 3a-5e. There is no significant variation in the thermal stability due to composition weight ratio of leather particulate – polymer. The temperature at which 10% weight loss occurs was denoted as T_{D10} as shown in the Figs. 3. The results indicate the thermal stability T_{D10} was found to be 225-275°C for different composites (C1, C3 and C5) as shown in Figure 3a-3c. Leather fiber – polymer binding and chromium present in the leather waste could contribute for the higher decomposition temperature. The nano-composites with nano fillers (C6 and C7) show increase in thermal stability of 330°C and 350°C respectively due to better reinforcement. Here, nano TiO₂ (<100 nm) provides better thermal stability than that of (20 nm) particle size.

Differential Scanning Calorimetry (DSC)

Differential scanning calorimetric analysis of the composites samples were performed with a *Du Pont DSC 2910* model thermal analyzer system (Delaware, US). DSC analysis was carried out under Nitrogen at atmosphere a heating rate of 10°C/min to analysis resin curing. The thermal behavior studies of the polymer blends could be one of the most effective methods for determining the Glass transition temperature (T_g) of the polymer. The same shall be expressed as in terms of T_g value for the resultant composite samples.²⁰ The extent of cured network structures formed could also be directly read from the T_g value of the cured resins. DSC scans of different leather particulate – polymer systems prepared are shown in Figure 4a-4e.

Accordingly, DSC scans of the cured polymers show a single T_g values, which confirmed that, these blends have formed homogeneous networks. The shrinkage values for the formulations C1 and C3 were found to be around 54°C and 76°C, as shown in Figs 4a and 4b respectively. DSC of the

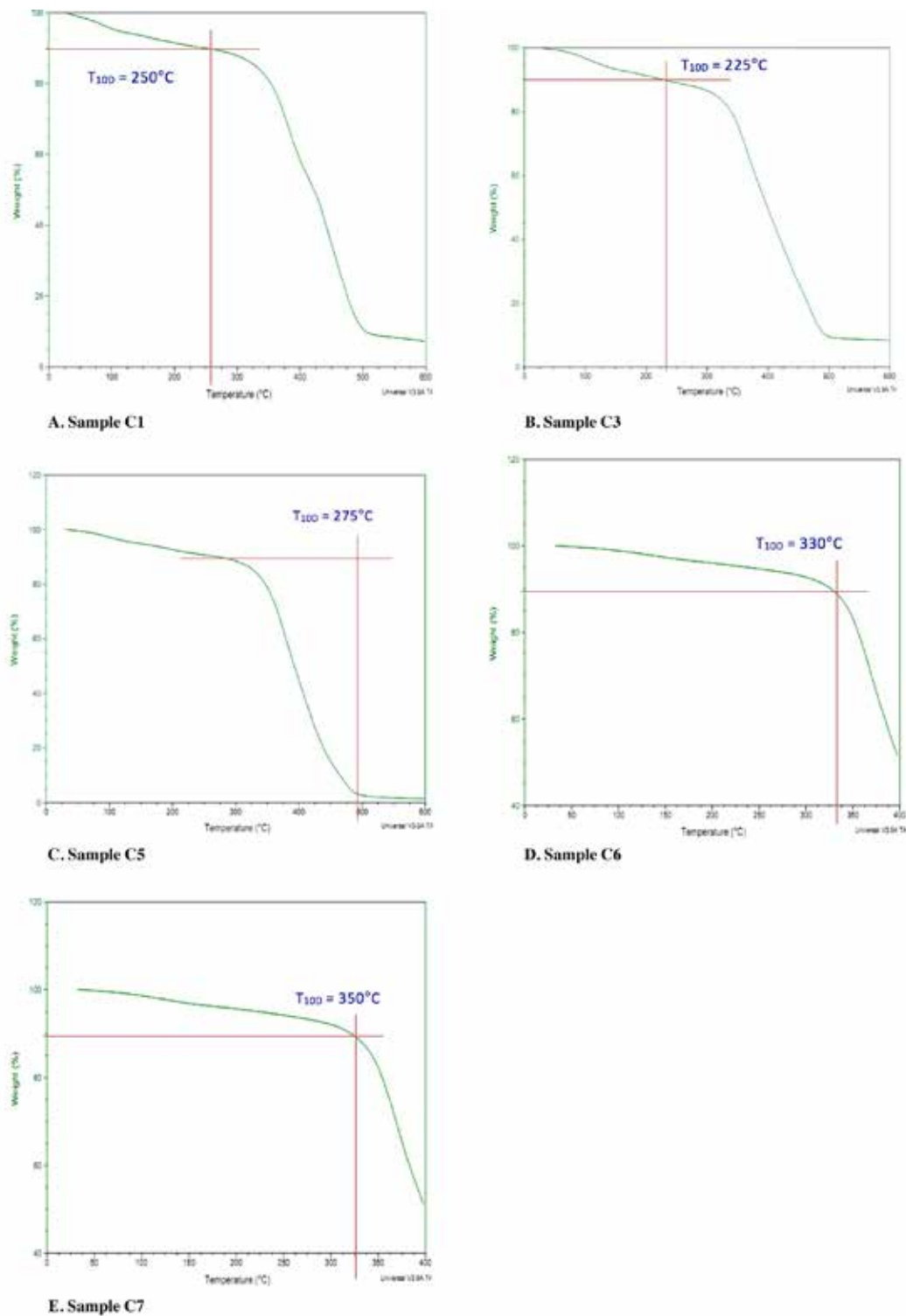


Figure. 3. TGA curve of the various composite and nano composite using epoxy- leather waste fibre.

other samples, i.e. C6, C7 indicate T_g value of 76°C and 75°C respectively as shown in Figs 4c and 4d respectively. The glass transition region is very narrow indicating a very limited compatibility between the blend components and also clearly suggests a possibility of distinct phase separation. At a higher

temperature the viscosity will be much less and the reaction between polymer and the hardener would be faster, and phase separations of the smaller particles will be more efficient. DSC curve of the epoxy polymer blank sample (C5) without leather fiber show T_g value of 75°C as shown in Figure 4e.

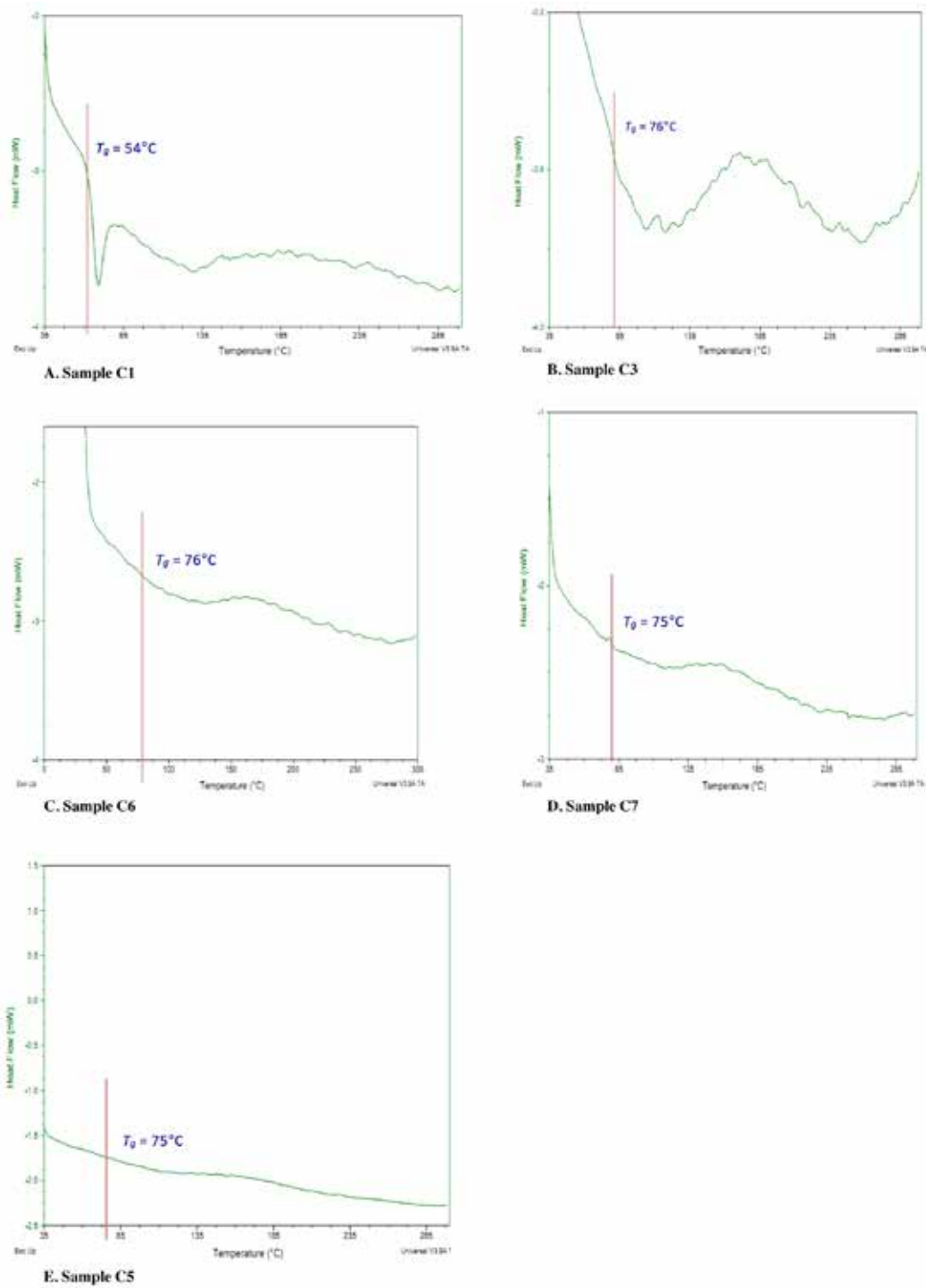


Figure. 4. DSC thermogram of the various composite and nano composite using epoxy- leather waste fibre.

Fourier Transform Infrared Spectroscopy (FT-IR)

Characterization of a polymer involves much more than the location of the ring bands and other bonding. There are many polymers with different structures, different polymerization degrees etc. IR spectroscopy can be used to characterize the nature of the polymer.^{21,22}

FT-IR spectra of leather particulate-polymers (Sample C1) is shown in Figure 5. Assignments for the various peaks are given in Table IV. The epoxide group linkage $-O-$ was confirmed by the presence of bands at 1246 cm^{-1} and 827 cm^{-1} , which accounts for the stretching of $C-O-C$ group. $C-N$ stretching at 1180 cm^{-1} and 1037 cm^{-1} could be accounted for the presence of leather

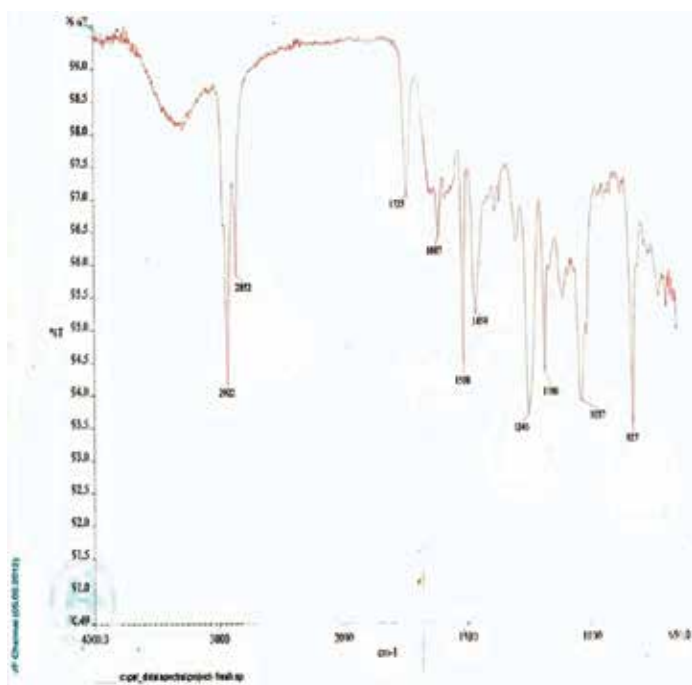


Figure 5. FT-IR spectra of leather fiber particulate-polymer composite (Sample C1).

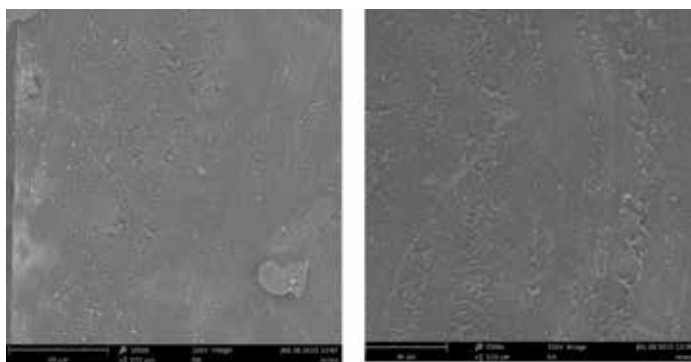


Figure 6. Scanning Electron Microscopic (SEM) images of cross section of nano-composite prepared using leather waste fibre and epoxy polymer (Figure 6a. Sample C6 using Nano TiO₂; Figure 6b. Sample C7 using Anatase nano TiO₂).

fibers. The FTIR spectral analysis showed that the Leather particulate – Polymer formulations have been cross-linked effectively. Presence of C–H/CH₂ stretching mode is confirmed from peaks at 2922, 2852 and 1459 cm⁻¹.

Chemical Resistance Test

Specimens with 0.5x0.5–cm size were cut from cured samples. These specimens were dried and weighed on balance. The weighed, measured samples were placed in specimen jars and then immersed in selected solvents such as acetone, aceto nitrile, ethyl acetate, hydrogen peroxide, methanol and sodium hydroxide. At the end of 24 hours the specimen was investigated for any physical change or dissolution. It was observed that there was no change in the specimen

TABLE IV
FT-IR analysis of Leather fiber – Epoxy composite and assignment for various peaks

FT-IR Peak (cm-1)	Assignment for the Groups
2922	CH/CH ₂ stretching
2852	CH/CH ₂ stretching
1735	C=O group
1607	C=C stretching of aromatic rings
1508	C-C stretching aromatic
1459	Defraction of C-H of CH ₂ /CH ₃
1246	Epoxy group
1180	C-N stretch (leather fiber)
1037	Stretching C-O-C of ether and C-N stretch
827	Stretching of C-O-C of oxirane group
<1000	Metal ions (Cr)

characteristics for nano-composite samples (C6 & C7) upon treatment with different solvents.

Scanning Electron Microscopic (SEM) Analysis

Micro structure of cross section of nano composites (using C6: Nano TiO₂ and C7: Anatase) has been studied using SEM analysis and shown in Figure 6a and 6b. The SEM analysis shows that homogeneity of the nano-composite matrix, composed of well mixed buffing dust and epoxy polymer with nano TiO₂ embedded as well as well distributed in the matrix seen as visible white dots in the SEM pictures. The SEM micrographs also indicate nano TiO₂ particles are distributed uniformly in the nano-composite matrix.

CONCLUSIONS

Large amount of leather waste fibers generated from the leather industries require proper attention. In this regard, leather fiber-epoxy nano-composite material was successfully prepared utilizing the buffing dust leather waste. Nano-composite was prepared comprising of epoxy polymer, nano-particles from defined particle size of leather waste fibers and

nano particles of titanium–di–oxide. Thus, it is envisaged to have potential application as lightweight construction material with requisite strength properties.

Leather particulate – polymer composite modified with nano fillers showed better tensile strength and hardness properties. This property was supported by the strong mechanical phase interaction brought by the chemical bonding with leather interface was confirmed by FTIR analysis. DSC and TGA revealed that better thermal stability up to 330°C for nano–composites prepared. A high chemical resistant property was observed which enables the application of composite material even under highly corrosive environments. From all the above mentioned features the nano–composite is capable of finding numerous applications. For example it could be used in fire resistant parts/ places, chemically corrosive environment, for construction due to high hardness and tensile properties and also for mechanical automobile body parts etc. SEM analysis indicates uniform nano-composite structure and distribution of nano TiO₂ in the nano-composite matrix. Thus, this study reveals that leather waste fiber material obtained in leather industry could be used for making useful nano–composites. This leather– polymer composite not only solves a disposal problem of leather solid wastes, such as buffing dusts, but also provides useful material for further beneficial use.

ACKNOWLEDGEMENTS

One of the Authors V.S thanks ZERIS Project (WP16) under XIIth plan project of CSIR–CLRI and also CSIR, New Delhi for the financial support in the research work.

REFERENCES

- Buljan, J., Reich, G., Ludvik, J.; Mass balance in leather processing, UNIDO Report, South Asia, 2000.
- Sutton, R., Production of polyurethane film/split leather laminate, US Patent: US 3713938A, 1970.
- Sivakumar, V., Gayathri, P.D., Amudha, T.; Ultrasound assisted acid red dye removal using leather fibre wastes as matrix: ‘Intra Wastes Interaction’ Approach. *Int. J. Env. Studies* **70**(4), 536-548, 2013.
- Sekaran, G., Shanmugasundaram, K.A., Mariappan, M.; Characterization and utilisation of buffing dust generated by the leather industry. *J. Hazard. Mater.* **63**(1), 53–68, 1998.
- Ozgunay, H., Colak, S.; Mutlu, M.M.; Akyuz, F.; Characterization of leather industry wastes. *Polish J. Environ. Studies* **16**(6), 867–873, 2007.
- Swarnalatha, S.; Srinivasulu, T.; Srimurali, M.; Sekaran, G.; Safe disposal of toxic chrome buffing dust generated from leather industries. *J. Hazard. Mater.* **150**(2), 2008, 290-299.
- Salwa, H.; El-Sabbagh.; Mohamed, O. A.; Recycling of chrome-tanned leather waste in acrylonitrile butadiene rubber. *J. Appl. Polym. Sci.* **121**(2), 979-988. 2011.
- Mohamed, O. A., El Sayed, N. H., Abdelhakim, A. A.; Preparation and characterization of polyamide-leather wastes polymer composites. *J. Appl. Polym. Sci.* **118**(1), 446-451. 2010.
- Vedaraman, N., Rangasamy, T., John Sundar V., Narashimasamy, T., Ganga Radhakrishnan., Muralidharan, C.; Buffing dust waste – A useful source for making leather like sheets. XXX IULTCS Congress, 2009, China.
- Rajaram, J., Rajnikanth, B., Gnanamani, A.; Preparation, characterization and application of leather particulate–polymer composites. *J. Polym. Environ.* **17**, 181–186, 2009.
- Richard, P., Prasse, T., Cavaille, J.Y., Chazeau, L., Gauthier, C., Duchet, J.; Reinforcement of rubbery polymer by carbon nanofibres. *Mater. Sci. Eng.* **A352**, 344–48, 2003.
- Tao, E., Hong-Rui, Ma and Yun, Li.; A Cleaner Al₂O₃-ZrO₂/MMT nanocomposite adsorbent based on Al-Zr tanning waste. *JALCA*, **109**, 39-396, 2014.
- Picagli, R.G., Tucker, E.S., Infantino, J.R., Light, H.J., Marinaccio, P.J.; Fiore J.V., European Patent EP0089029, 1983.
- Schmidt, H.; Composite materials, U.S Patent No 6,287,639, 2001.
- Coulson, N.S., Kilnsley, H.B., Nunn, J.K.; Composite leather material, PCT Patent No. WO2007047848, 2006.
- Ramaraj, B.; Mechanical and Thermal Properties of ABS and Leather Waste Composites. *J. Appl. Polym. Sci.* **101**, 3062–3066, 2006.
- Ambro’sio, J.D., Lucas, A.A., Otaguro, H., Costa, L.C.; Preparation and characterization of poly (vinyl butyral) – leather fiber composites. *Polym. Compos.* **32**(5), 776-785, 2011.
- Zeng, J., Schlup, J.R., Fan, L.T.; Synthesis and mechanical properties of leather–epoxy interpenetrating polymer network. *J. Appl. Polym. Sci.* **78** (2000) 1224–1232.
- Sivakumar, V., Mandal, A.B.; CSIR, Leather fiber epoxy nano composite material for industrial applications and a process for the preparation thereof, Indian Patent Ref. No. 2893DEL2014, 2014.
- Kim, H., Whisler, D., Chen, Z.M., Bisagni, C., Kawai, M., Krueger, R.; Proceedings of the American Society for Composites 2014-Twenty-ninth Technical conference on composite Materials, DEStech Publications Inc., 2014, pp.128-132.
- Coates, J., Interpretation of Infrared Spectra, A practical approach, encyclopedia of analytical chemistry, R.A. Meyers (Ed.), John Wiley & Sons Ltd, Chichester, 2000, pp. 10815–10837.
- González, M.G., Cabanelas, J.C., Baselga, J.; In: Infrared Spectroscopy - Materials Science, Engineering and Technology, Theophanides, T., (Ed.), InTech publication, Croatia, 2012, Chapter 13.