

Preparation and Characterization of Composite Sheets from Collagenous and Chromium–Collagen Complex Wastes Using Polyvinylpyrrolidone: Two Problems, One Solution

M. Ashokkumar · P. Thanikaivelan ·
R. Murali · B. Chandrasekaran

Received: 5 April 2010 / Accepted: 18 June 2010 / Published online: 27 June 2010
© Springer Science+Business Media B.V. 2010

Abstract The disposal of huge quantities of leather wastes in open environment produces several toxic contaminants. An alternative to disposal of these wastes is to reuse them. In the present work, we have proposed a method to utilize collagen and chrome shaving wastes (CCS) to prepare composite sheets employing polyvinylpyrrolidone (PVP). The formed CCS/PVP composite sheets were characterized for their thermal, mechanical and morphological properties. It has been found that the mechanical properties of the composite sheets increase as the concentration of PVP increases from 2.5 to 10 wt%. Scanning electron microscopic studies reveal that the incorporation of PVP in the composite sheets resulted in increased interfacial adhesion thereby leading to reduced debonding between fibers. Fourier-transform infrared analysis of the composite sheets revealed the presence of dominant peaks associated with both collagen as well as PVP. It has also been demonstrated that the thermal stability of the formed composite sheets increases significantly as the concentration of PVP increases. These results demonstrate the homogeneity of the developed composite sheets. The obtained results suggest that the PVP incorporated composite sheets were found to have improved characteristics and hence suitable for numerous applications in footwear, clothing and related industries.

Keywords Composites · SEM · Wastes · Mechanical property · Thermal property

Introduction

The transformation of hides into leather requires a series of chemical and mechanical operations [1, 2]. The generation of solid wastes during leather manufacturing is unavoidable. The solid wastes generated from leather industry can be broadly classified as untanned collagenous, tanned collagen–chromium complex and non-proteinous wastes. The deposition of huge quantity of tanned collagen–chromium complex wastes in land is a potential danger to public health due to the possibility of oxidation of chromium(III) into toxic chromium(VI) [3]. Chromium(VI) has been shown to cause serious toxic and carcinogenic effect leading to respiratory, lung, skin and bladder cancer [4–8]. Proper recycling of these wastes would certainly save the energy and conserve the resources. However, only limited eco-friendly processes were developed from leather wastes because of the presence of hazardous chemicals or ingredients [9]. Hence, there is a need to develop cleaner processes in order to find a practical solution to the disposal of this potentially toxic waste.

Several researchers have attempted to improve the valorization of skin and leather wastes. Most methods for leather waste treatment aim at recovery and isolation of protein fraction, which are generally based on the alkaline hydrolysis using CaO, MgO, NaOH [10–17], acidic hydrolysis [18] or enzymatic hydrolysis [12, 19, 20]. Direct use of the solid leather wastes was also studied for their ability to remove oils, oily wastes and hydrocarbons from contaminated water [21]. Ceramic materials prepared with alumina and ashes of chrome tanned shavings were

M. Ashokkumar · P. Thanikaivelan (✉) · R. Murali ·
B. Chandrasekaran (✉)
Advanced Materials Laboratory, Centre for Leather Apparel
and Accessories Development, Central Leather Research
Institute (Council of Scientific and Industrial Research), Adyar,
Chennai 600020, India
e-mail: thanik8@yahoo.com

B. Chandrasekaran
e-mail: cladclri@yahoo.com

reported [22]. The effect of incorporation of chromium leather shavings in the preparation of Portland cement clinker was studied [23].

The development of composite materials using polymers is one of the alternative ways for the management of solid leather wastes such as chrome shavings and buffing dusts. The chrome tanned leather shavings were used after multi-step disintegration, to prepare a powder, which were used as filler of butadiene-acrylonitrile rubber [24]. Several patents were filed for converting the leather wastes into sheet or boards for a variety of applications [25–30]. Chrome-tanned waste collagen was used, beside silica, as a filler of rubber mixes containing synthetic 1,4-*cis*-polyisoprene rubber and as dispersing agent [31]. The polymerization of poly methyl methacrylate onto leather wastes to form composites sheets was reported [32–34]. This modification is claimed to improve the finishing, dyeing and stability of the formed composite sheets. Santana et al. [35, 36] prepared composite sheets by addition of polyvinyl chloride (PVC) with leather waste. The leather wastes were used as filler [37] in thermoplastic polymer composite to increase their mechanical and thermal properties. Chemically modified short leather fibers were compression molded into plasticized PVC matrix [38], di-octyl phthalate plastisols [39, 40] to form composites with improved properties. Efforts were made to form polymer composites using chromium containing wastes with butadiene rubber [41] and PVC [9], which were found to have improved properties.

The present work aims at utilizing collagenous wastes and chromium containing collagenous wastes for making composite sheets with polyvinylpyrrolidone (PVP). Further, the mechanical properties of the developed polymer composite sheets were studied by analyzing their tensile strength and elongation at break. Morphology of the broken samples after tensile testing was analyzed using scanning electron microscopic analysis, while thermal properties were analyzed by differential scanning calorimetric and thermogravimetric analysis. Fourier-transform infrared (FT-IR) analysis of the developed composite sheets was also carried out to find out the efficiency of the developed process to form homogeneous sheets.

Materials and Methods

Materials

Chrome tanned leather shaving wastes (CS) and collagenous wastes (C) [untanned skin trimming wastes] were obtained from a local tannery. Glacial acetic acid and sulphuric acid were obtained from M/s Rankem chemicals, India and the polyvinylpyrrolidone was purchased from M/s Himedia chemicals, India.

Preparation of Skin Powder

The raw skin trimmings were soaked in 300% (v/wt) water for 2 h. The process was repeated twice. The soaked skin pieces were limed, dehaired, relimed, fleshed and delimed completely using conventional procedures. Finally, the skin pieces were thoroughly dried in a vacuum drier. The completely dried skin pieces were grounded finely into powder using a Willy mill of mesh size 2 mm.

Formation of Composite Sheets

A known weight of skin powder was soaked in 3000% (v/wt) 0.5 N acetic acid for 4 h and then ground finely using a blender to form collagenous paste (C). A known weight of chrome shavings (CS) was soaked in 500% (v/wt) 2.5 N sulphuric acid and 500% (v/wt) water for 4 h. The soaked chrome shavings were squeezed out of the water-sulphuric acid mixture and grounded finely to form a viscous mass using a blender.

The above formed collagenous paste (C) and chrome shaving mass (CS) were mixed together in a constant ratio of 1:10 (on raw weight basis) to form a homogenous mixture (CCS). To this mixture, polyvinylpyrrolidone (PVP) was added in different ratios such as 2.5, 5, 7.5 and 10 wt%. The contents were mixed finely to form a homogenous paste using blender. The formed homogenous pastes were transferred to non-stick sheets and hot-pressed into sheets of even thickness under 2.4 MPa. The CCS/PVP composite sheets were kept at $40 \pm 5^\circ\text{C}$ for 5 min during hot-pressing. The formed CCS/PVP composite sheets were left to dry at room temperature.

Mechanical Testing

Mechanical properties of the developed CCS/PVP composite sheets were carried out using an Instron 4501 Universal testing machine. The composite sheets were cut into dumb-bell shape specimens of size 40×5 mm (length: width) and measured according to ASTM standard D882 [42]. The tests were carried out using 1 kN load cell and the crosshead speed was set at 50 mm/min. The final mechanical properties of composite sheets were evaluated from the average of three samples from each experiment.

Thermal Analysis

The thermal properties of the developed CCS/PVP composite sheets were characterized using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The DSC analysis of the composite sheets was carried out using Perkin-Elmer DSC Q200 V23.10 Build 79, in the presence of nitrogen atmosphere and at the heating rate of

10°C/min from 0 to 300°C. The TGA analysis was carried out using Perkin-Elmer TGA Q50 V20.6 Build 31, in the presence of nitrogen atmosphere. About 5 to 10 mg of samples were heated from 0 to 800°C at a heating rate of 20°C/min.

FT-IR Analysis

Fourier-transform infrared measurements were performed on a FT-IR Perkin-Elmer spectrometer, operating in normal transmission mode. The CCS/PVP composite sheets were ground finely with KBr and pressed to form pellets. The formed pellets were analyzed over the range of 400–4000 cm^{-1} at a resolution of 2 cm^{-1} with an average of 12 scans. All the spectra were baseline corrected and normalized. No other processing was performed on the spectra.

Scanning Electron Microscopic (SEM) Analysis

The fractured surfaces during tensile strength of the CCS/PVP composite sheets were observed using a FEI Quanta 200, environmental scanning electron microscope. The composite sheets were coated with gold using an Edwards E306 sputter-coater. The micrographs were obtained at an accelerating voltage of 20 kV and at different magnifications.

Softness Analysis

The softness of composite sheets was analyzed using a ST 300 digital leather softness tester employing standard procedure [43]. The size of reducing ring was 25 mm. The distension of composite sheets was measured and the softness was expressed in mm. The average values of three samples from each experiment were calculated.

Moisture Content

The moisture content of composite sheets was analyzed following standard procedure [42]. Composite sheets were weighed (w_1), dried at 100°C for 5 h, and weighed (w_2) again. Moisture content (MC) was determined using the following equation.

$$\text{MC (\%)} = 100(w_1 - w_2)/w_1$$

Three specimens were used for each type of composite sheets and the average value was calculated.

Thickness Measurement

Thickness of the composite sheets was measured following standard procedure [44]. Thickness was determined using a bench type thickness gauge (S.No.2201.2.4, Baker, India) to the nearest 0.01 mm at 3 random positions around the composite sheets and average values were calculated.

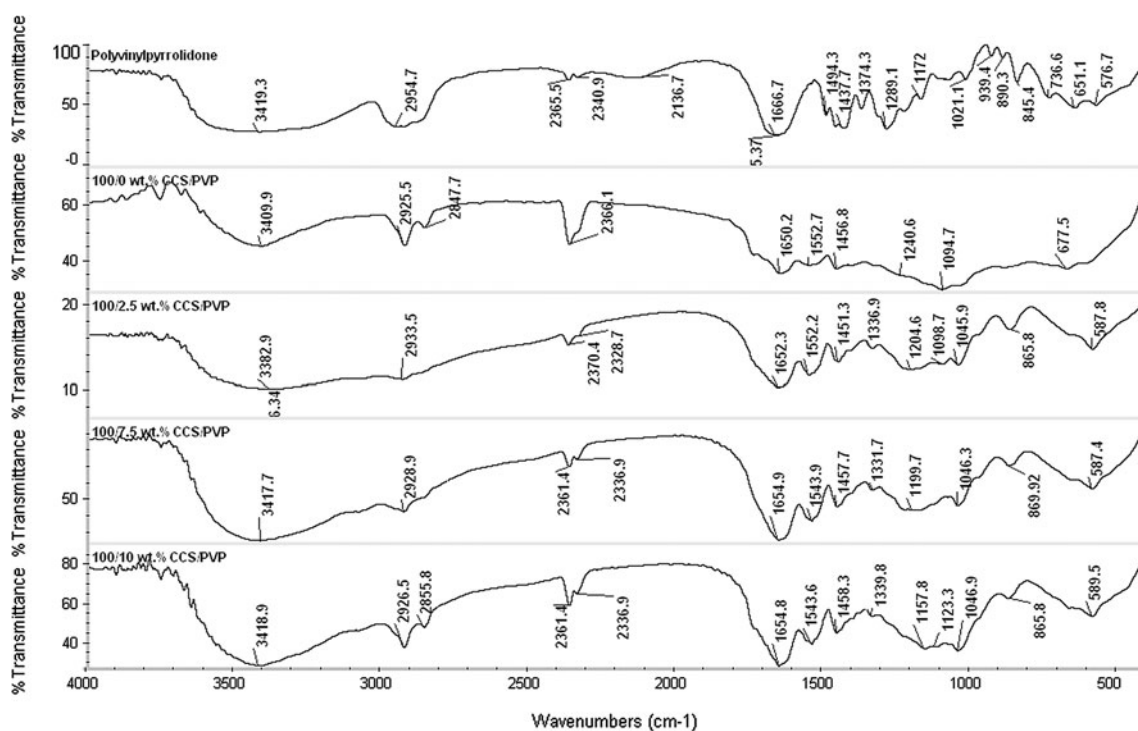
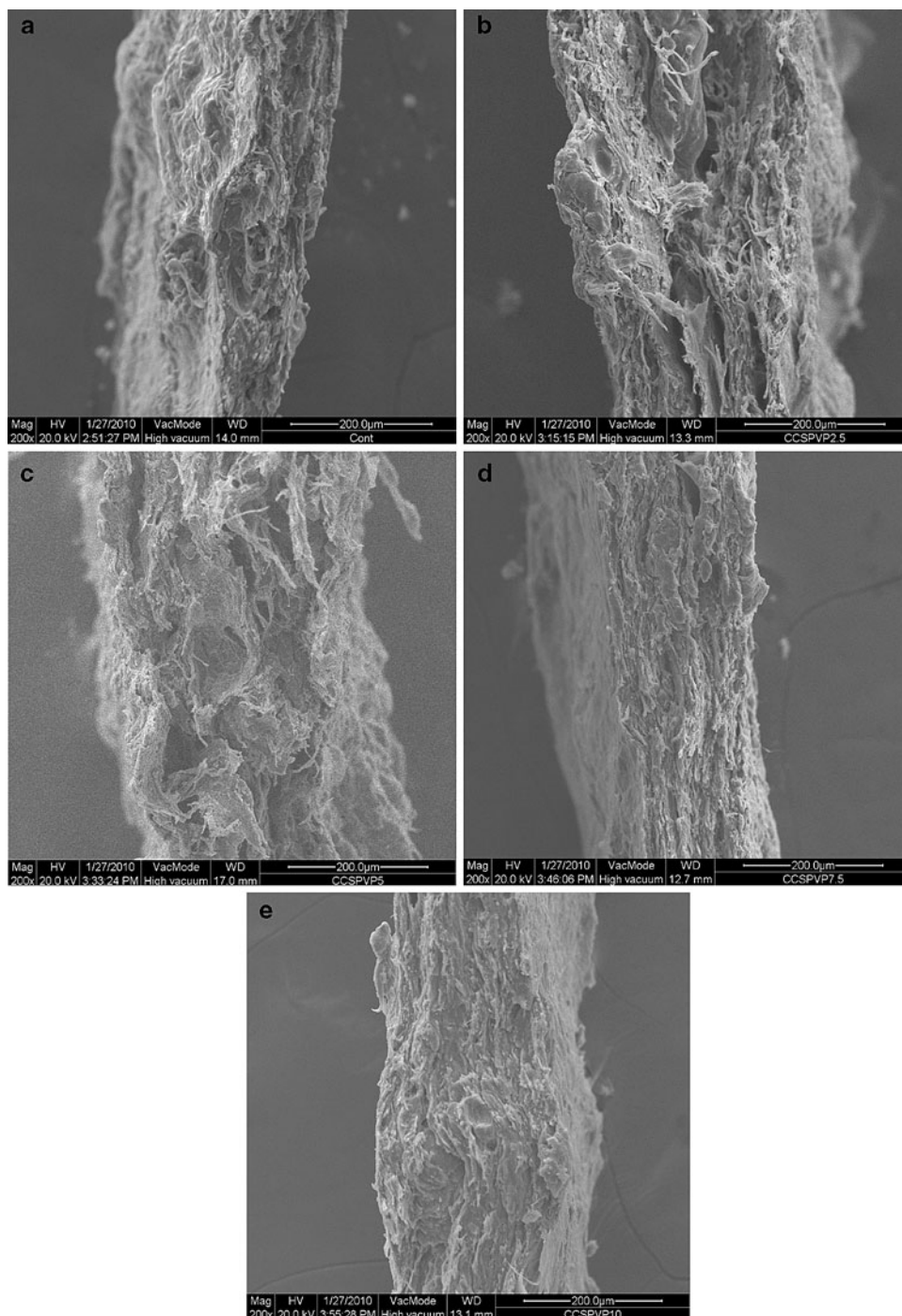


Fig. 1 FTIR spectra of the select CCS/PVP composite sheets

Fig. 2 Scanning electron photomicrographs of broken edges of different CCS/PVP composite sheets at a magnification of 200 \times ; **a** 100/0 wt% CCS/PVP, **b** 100/2.5 wt% CCS/PVP, **c** 100/5 wt% CCS/PVP, **d** 100/7.5 wt% CCS/PVP and **e** 100/10 wt% CCS/PVP



Results and Discussion

FT-IR Analysis

Figure 1 shows the infrared spectra of PVP and CCS/PVP composite sheets. The characteristic peaks of PVP are seen at 2954, 1666, 1437, 1374, 1289, 576 and 845 cm^{-1} corresponding to C–H stretching, C=O stretching, CH_2 scissoring, C–C ring stretching, C–N stretching, N–C=O bend,

ring deformation and C–C stretching [45]. Since the chrome shavings originate from skin/hides, it possesses the characteristic peaks corresponding to collagen. In the IR spectrum of collagen-chrome shaving mixture, the bands at 1650, 1552 and 1240 cm^{-1} correspond to amide I, II and III bands of collagen [46]. The amide I absorption arises predominantly from C=O stretching vibrations while the amide II absorption is from N–H and C–N vibrations. The amide III peak is complex, consisting of components from

Fig. 3 Scanning electron photomicrographs of broken edges of different CCS/PVP composite sheets at a magnification of 800 \times ; **a** 100/0 wt% CCS/PVP, **b** 100/2.5 wt% CCS/PVP, **c** 100/5 wt% CCS/PVP, **d** 100/7.5 wt% CCS/PVP and **e** 100/10 wt% CCS/PVP

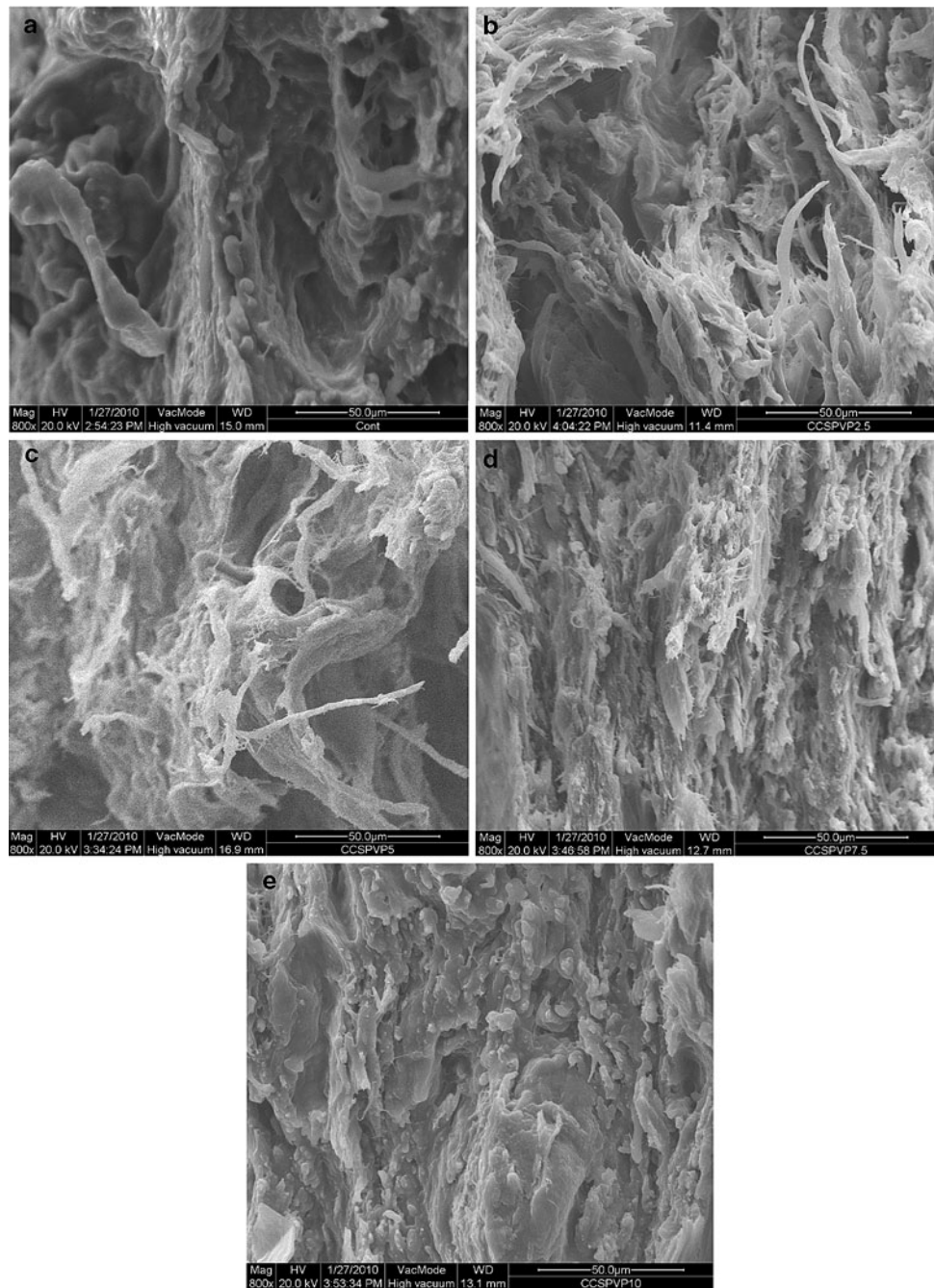


Table 1 Mechanical properties and softness of CCS/PVP composite sheets

Composition of CCS/PVP composite sheets (wt%)	Load (N)	Stress (MPa)	Strain (%)	Thickness (mm)	Softness (mm)	Moisture content (%)
100/0	7.01 \pm 1.3	7.37 \pm 2.2	1.87 \pm 0.6	0.3 \pm 0.15	2.13 \pm 0.2	18.2 \pm 1.0
100/2.5	8.83 \pm 0.91	9.28 \pm 1.8	2.3 \pm 0.4	0.3 \pm 0.12	3.51 \pm 0.1	17.2 \pm 0.5
100/5	16.79 \pm 1.1	17.47 \pm 0.7	2.7 \pm 0.5	0.3 \pm 0.15	1.95 \pm 0.1	16.4 \pm 0.5
100/7.5	26.67 \pm 1.7	18.90 \pm 1.2	4.74 \pm 0.1	0.3 \pm 0.1	1.69 \pm 0.0	16.1 \pm 1.0
100/10	30.93 \pm 0.09	21.31 \pm 5.9	4.85 \pm 0.2	0.3 \pm 0.1	1.52 \pm 0.0	15.8 \pm 0.5

C–N stretching, N–H in-plane bending as well as absorptions arising from wagging vibrations from CH₂ groups. The amide III peak is observed with smaller peak at 1240 cm⁻¹.

It is interesting to note that the C=O stretching (1650 cm⁻¹) band becomes broader and deeper as the concentration of PVP increases in the CCS/PVP composite sheet. This may be due to the incorporation of higher amount of PVP content into the composite sheet. In addition to this, some of the characteristic peaks of PVP are pronounced moderately in the CCS/PVP composite sheets, which were absent in 100/0 wt% CCS/PVP composite sheet. Especially, the peaks around 1336 cm⁻¹ (C–C ring stretch), 865 cm⁻¹ (C–C stretch) and 587 cm⁻¹ (N–C=O bend, ring deformation) were seen only in the PVP incorporated composite sheets. These results indicate the homogenous mixing and incorporation of PVP with the CCS mass.

Fractured Surface Analysis

The fractured surface of the developed CCS/PVP composite sheets at a lower magnification 200× is shown in Fig. 2. It is seen that more fibre pull-out is exhibited by 0, 2.5 and 5 wt% CCS/PVP composite sheets compared to 7.5 and 10 wt% CCS/PVP composite sheets. Large fibre bundles and a number of individual fibres can be seen extending from the fractured surface of the CCS/PVP composite sheets with lower proportion of PVP (0, 2.5 and 5 wt%), which may be due to the less binding nature of the PVP at lower proportions. The fibre pull-out has been found to be reduced significantly as the concentration of PVP increased above 5 wt%.

Higher magnification scanning electron micrographs of fractured CCS/PVP composite sheets are shown in Fig. 3. As noted in lower magnification micrographs, the fiber pull-out is clearly visible in the composite sheet with lower proportion of PVP (2.5 and 5 wt%). On the other hand, the composite sheets with 100/7.5 and 100/10 wt% CCS/PVP composition show short fiber pull-out length with reduced microfibrillar structure [38]. These results indicate the incorporation of PVP with chromium-collagen matrix with increased binding.

Mechanical Properties

The tensile strength of CCS/PVP composite sheets as a function of an increase in the PVP concentration is presented in Table 1. It is observed that the mechanical properties of the developed CCS/PVP composite sheets are enhanced with the increase in PVP concentration from 0 to 10 wt%. Especially, the tensile strength and elongation at break values of the developed CCS/PVP composite sheets are improved

considerably as the concentration of PVP increases in the composite sheets. This is primarily attributed to the strong reinforcement of PVP with the CCS mass. The composite sheet with 100/0 wt% CCS/PVP composition exhibits the least strength while the composite sheet with 100/10 wt% CCS/PVP composition displays 300% increase in the tensile strength. Low mechanical properties of CCS/PVP composite sheets with low proportion of PVP (0 and 2.5 wt%) may be due to the inadequate quantity of PVP leading to less binding of the PVP with CCS mass. The less binding characteristic exhibited by 100/0 and 100/2.5 wt% CCS/PVP composite sheets is also supported from SEM analysis where long pull-out of fibers and more micro-fibrillar formation are visible. It is seen that ≥5 wt% PVP concentration is sufficient to provide CCS/PVP composite sheets with increased mechanical properties. Moreover, the incorporation of PVP into CCS mass reduces fibre-matrix debonding that often leads to the formation of micro voids or microfibrillar structure thus further weakening the overall composite performance. The absence of microfibrillar structure and long fiber pull-out length as observed from SEM images of the CCS/PVP composite sheets with higher composition of PVP (7.5 and 10 wt%) corroborate well with these mechanical property results. The softness values of the developed CCS/PVP composite sheets are shown in Table 1. It is seen that the softness property of formed CCS/PVP composite sheets decreases gradually as the concentration of PVP increases. The softness values and tensile strength values of the developed composite sheets exhibit an inverse relationship. The composite sheets (0, 2.5 and 5 wt% CCS/PVP) with good softness exhibit less tensile strength, while those with low softness (7.5 and 10 wt% CCS/PVP) show higher tensile strength. It is also seen from Table 1 that the moisture content of the developed CCS/PVP composite sheets ranges between 16 and 18%. Higher moisture content in the

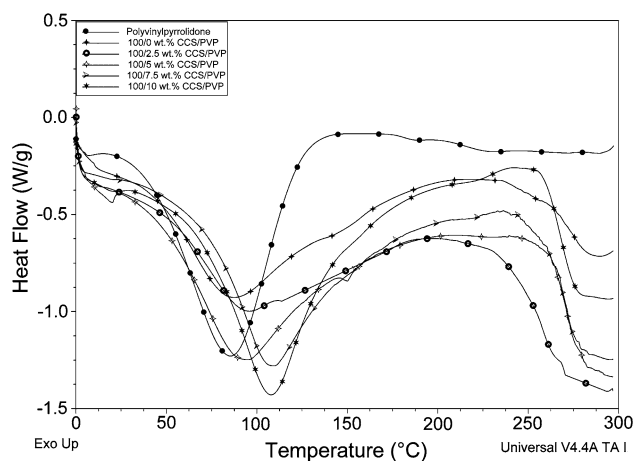


Fig. 4 DSC thermograms of the CCS/PVP composite sheets

composite sheets is generally due to the high hydrophilic nature of collagen, chromium-collagen complex and PVP.

Differential Scanning Calorimetric Analysis

DSC scans of PVP and CCS/PVP composite sheets are shown in Fig. 4. When PVP was blended with CCS (collagen-chrome shaving) mass, a single endothermic transition in the temperature range of 80–110°C was exhibited. As the content of PVP increased, the endothermic curve of CCS/PVP composite sheet became more prominent. This endotherm of PVP and CCS/PVP composite sheets may be attributed to the presence of absorbed moisture or water molecules. Addition of PVP increased the heat flow, which

may be due to the superior hydrophilic character of PVP with the CCS mass. No additional endothermic transition was observed for the CCS/PVP composite sheets up to 300°C.

Thermogravimetric Analysis

The TGA thermogram of PVP and different CCS/PVP composite sheets are shown in Fig. 5. Polyvinylpyrrolidone shows a single stage decomposition with an inflection point of 450°C, corresponding to the decomposition of polymer matrix. The weight loss of PVP is around 87%. All the CCS/PVP composite sheets exhibit two-stage weight loss. The first stage occurs around 80–120°C, which may be due

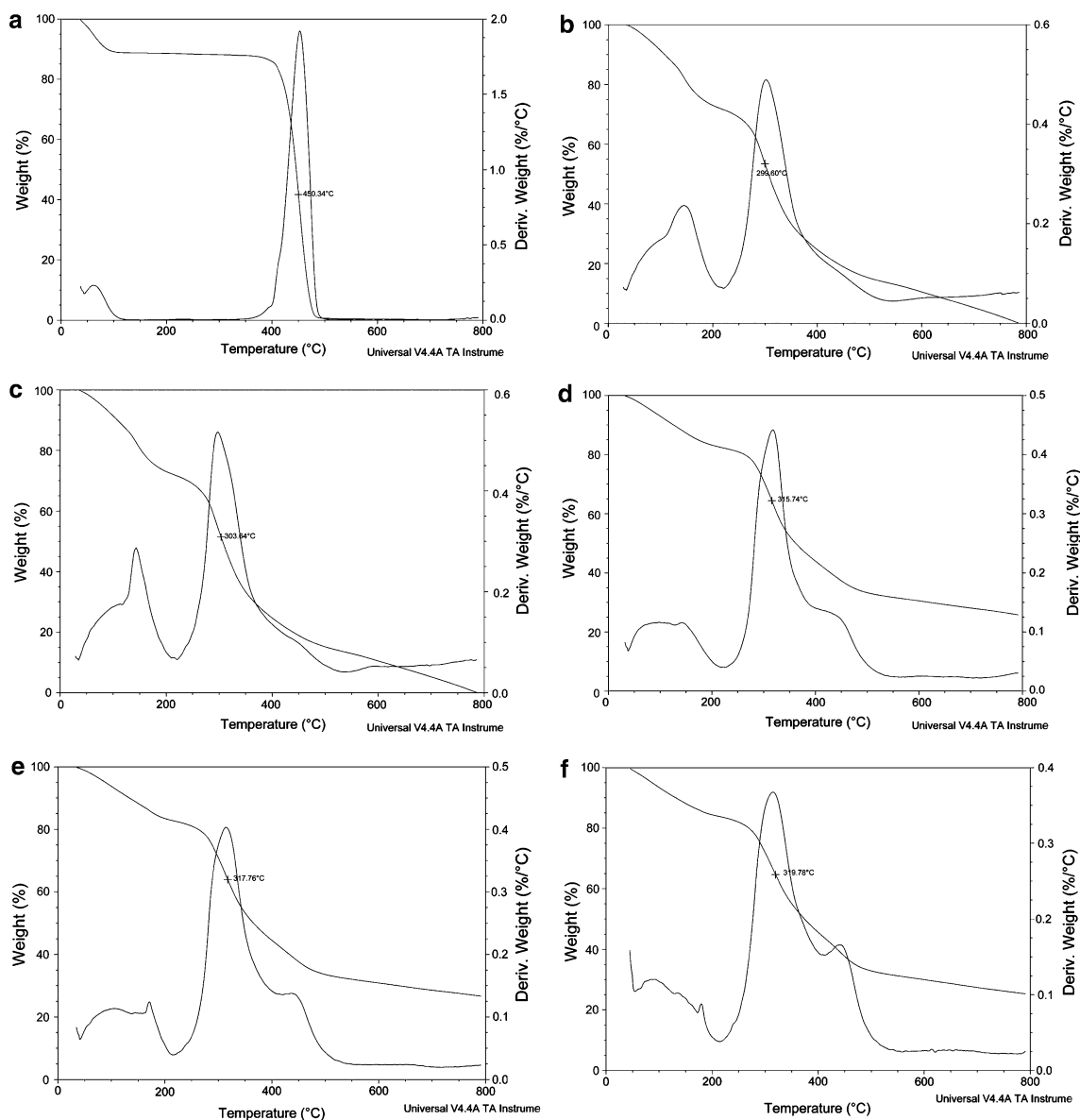


Fig. 5 TGA curves of the developed CCS/PVP composite sheets. **a** PVP, **b** 100/0 wt% CCS/PVP, **c** 100/2.5 wt% CCS/PVP, **d** 100/5 wt% CCS/PVP, **e** 100/7.5 wt% CCS/PVP and **f** 100/10 wt% CCS/PVP

to the loss of absorbed moisture content present in the CCS/PVP composite sheets. The first stage indicating the presence of absorbed moisture was well supported by DSC results.

The second stage representing the decomposition of CCS/PVP composite sheets starts at 220°C and continues up to 550°C. The decomposition temperature was found to be 301°C for 100/0 wt% CCS/PVP composite sheet (Fig. 5b). The decomposition temperature of CCS/PVP composite sheets increases gradually as the concentration of PVP increases and reaches a maximum of around 320°C for 100/10 wt% CCS/PVP composite sheets (Fig. 5f). Interestingly, the CCS/PVP composite sheets with higher concentrations of PVP (≥ 5 wt%) exhibit a secondary decomposition inflection point around 450°C corresponding to the decomposition of the macromolecular structure of PVP as also evidenced from Fig. 5a. This clearly demonstrates that the incorporation of PVP into CCS enhanced the thermal stability of the formed CCS/PVP composite sheets. These results are in good agreement with the mechanical property and SEM analysis results.

Conclusion

In the present work, a possible solution for the management of different types of solid wastes generated from leather manufacturing industries has been developed. The addition of PVP with collagen-chrome shaving mass improved the characteristic properties of formed CCS/PVP composite sheets. Especially, the mechanical and thermal properties of the developed CCS/PVP composite sheets are improved considerably as the proportion of PVP increases in the composite sheets. On the other hand, the softness property decreases with increasing concentration of PVP. It is interesting to note from SEM analysis that the fiber pull-out and microfibrillar structure were minimized in the composite sheets with high PVP composition (7.5 and 10 wt%). SEM results are in agreement with the mechanical property results. The FTIR spectra of CCS/PVP composite sheets show characteristic bands corresponding to both collagen and PVP. These results indirectly demonstrate the homogeneous nature of the formed CCS/PVP composite sheets. The developed CCS/PVP composite sheets could be used as a replacement of leather-like materials in numerous applications. Nevertheless, a semi-technical level study would be required before attempting to commercialization in order to establish a techno-economic feasibility since the developed process requires considerable energy.

Acknowledgements The authors gratefully thank the Council of Scientific and Industrial Research (CSIR), India for providing financial assistance under YSA project scheme. The authors also thank

Mrs. G. Safi and Ms D.R. Jini for their valuable help and contributions in carrying out some of the experiments.

References

- Cassano, A., Drioli, E., Molinari, R.: Recovery and reuse of chemicals in unhairing, degreasing and chromium tanning processes by membranes. *Desalination* **113**, 251–261 (1997)
- Cassano, A., Drioli, E., Molinari, R.: Saving of water and chemicals in tanning industry by membrane processes. *Water Res.* **4**, 443–450 (1999)
- Aceves, M.B., Velasquez, R.O., Vazquez, R.R.: Effect of Cr^{3+} , Cr^{6+} and tannery sludge on C and N mineralization and microbial activity in semi-arid solids. *J. Hazard. Mater.* **143**, 522–531 (2007)
- Stern, F.B., Beaumont, J.J., Halperin, W.E., Murthy, L.I., Hills, B.W., Fajen, J.M.: Mortality of chrome leather tannery workers and chemical exposures in tanneries. *Scand. J. Work. Environ. Health* **13**, 108–117 (1987)
- Heidemann, E.: Disposal and recycling of chrome-tanned materials. *J. Am. Leather Chem. Assoc.* **86**, 331–333 (1991)
- Cabeza, L.F., Mcaloon, A.J., Yee, W.C., Taylor, M.M., Brown, E.M., Marmer, W.N.: Process simulation and cost estimation of treatment of chromium-containing leather waste. *J. Am. Leather Chem. Assoc.* **93**, 2990–3135 (1998)
- Dayan, A.D., Paine, A.J.: Mechanisms of chromium toxicity, carcinogenicity and allergenicity: review of the literature from 1985 to 2000. *Hum. Exp. Toxicol.* **20**, 439–451 (2001)
- Costa, M.: Toxicity and carcinogenicity of Cr(VI) in animal models and humans. *Crit. Rev. Toxicol.* **27**, 431–442 (1997)
- Rajaram, J., Rajinikanth, B., Gnanamani, A.: Preparation, characterization and application of leather particulate-polymer composites. *J. Polym. Environ.* **17**, 181–186 (2009)
- Tahiri, S., Bouhria, M., Albizane, A., Messaoudi, A., Azzi, M., Alami, S.Y., Mabrou, J.: Extraction of proteins from chrome shavings with sodium hydroxide and reuse of chromium in the tanning process. *J. Am. Leather Chem. Assoc.* **99**, 16–25 (2004)
- Brown, M., Taylor, M.M., Marmer, W.N.: Production and potential uses of coproducts from solid tannery waste. *J. Am. Leather Chem. Assoc.* **91**, 270–276 (1996)
- Mu, C.D., Lin, W., Zhang, M.R., Zhu, Q.: Towards zero discharge of chromium containing leather waste through improved alkali hydrolysis. *Waste Manag.* **23**, 835–843 (2003)
- Guardini, G.: Extraction of proteins and chromium sulphate from chromium tanned skin waste. U.S. Patent 4,483, 829 (1983)
- Holloway, D.F.: Recovery and separation of nutritious proteins hydrolysates and chromium from chrome leather scrap. U.S. Patent 4,100,154 (1978)
- Galatik, A., Duda, J., Minarik, L.: Pressure hydrolysis of leather waste with sodium hydroxide. Czech Patent CS 252, 382 (1988)
- Tahiri, S., Azzi, M., Albizane, A., Messaoudi, A., Bouhria, M., Alami, Y.S., Mourid, A., Amrhar, J.: Study of quality of a pigment prepared by complexation of chromates recovered from treated chrome shavings and tanned splits. *J. Am. Leather Chem. Assoc.* **96**, 426–436 (2001)
- Berry, F.J., Constantini, N., Smart, L.E.: Synthesis of chromium-containing pigment from chromium recovered from leather waste. *Waste Manag.* **22**, 761–772 (2002)
- Wojciech, L., Mieczyslaw, G., Urszula, M.: Leather treatment to remove chromium. PCT Int. Appl. WO 9803685 (1998)
- Taylor, M.M., Diefendorf, E.J., Marmer, W.N., Brown, E.M.: Effect of various alkalinity-inducing agent on chemical and physical properties of protein isolated from chromium-containing leather waste. *J. Am. Leather Chem. Assoc.* **89**(7), 221–228 (1994)

20. Cabeza, L.F., Taylor, M.M., DiMaio, G.L., Brown, E.M., Marmer, W.N., Carrio, R., Celma, P.J., Cot, J.: Processing of leather waste pilot scale studies on chrome shavings. Isolation of potentially valuable protein products and chromium. *Waste Manag* **18**, 211–218 (1998)
21. Gammoun, A., Tahiri, S., Albizane, A., Azzi, M., Moros, J., Garrigues, S., Guardia, M.D.L.: Separation of motor oils, oily wastes and hydrocarbons from contaminated water by sorption on chrome shavings. *J. Hazard. Mater.* **145**, 148–153 (2007)
22. Basesgio, T., Haas, C., Pokorny, A., Bernardes, A.M., Bergmann, C.P.: Production of materials with alumina and ashes from incineration of chromium tanned leather shavings: environmental and technical aspects. *J. Hazard. Mater.* **137**, 1156–1164 (2006)
23. Trezza, M.A., Scian, A.N.: Waste with chrome in the Portland cement clinker production. *J. Hazard. Mater.* **147**, 188–196 (2007)
24. Przepiorkowska, A., Chronska, K., Zaborski, M.: Chrome-tanned leather shavings as a filler of butadiene-acrylonitrile rubber. *J. Hazard. Mater.* **141**, 252–257 (2007)
25. Mathieu, A.N.: Improvement in the manufacture of leather paste board and paper. U.S. Patent 20,020 (1868)
26. Horowitz, A.R., Brooklyn, N.Y.: Method for the treatment and utilization of scrap or waste leather. U.S. Patent 2,148,904 (1939)
27. Case, A.W.: Manufactured leather. U.S. Patent 878,485 (1908)
28. Coulson, N.S., Kinsley, H.B., Nunn, J.K.: Composite leather material. U.S. Patent Appl. US2007/0184742A1 (2007)
29. Pelzer, H.: Moulded articles with leather-like surface properties for use in the automobile industry. U.S. Patent 5, 624, 619 (1997)
30. Henke, E.W.: Reconstitute leather and method of manufacturing same. U.S. Patent 4,497,871 (1985)
31. Przepiorkowska, A., Prochon, M., Zaborski, M.: Use of waste collagen as a filler for rubber compounds. *J. Soc. Leather Technol. Chem.* **88**, 223–227 (2004)
32. Klasek, A., Simonikova, J., Pavelka, F.: Grafting of 2-hydroxyethyl methacrylate and methyl methacrylate onto chrome tanned collagen fibers. *J. Appl. Polym. Sci.* **31**, 2007–2019 (1986)
33. Santana, T.J.M., Moreno, F.V.: Graft polymerization of methyl methacrylate onto short leather fibers. *Polym. Bull.* **42**, 329–336 (1999)
34. Jordan, E.F., Feairheller, S.F.: Polymer–leather composites II. Kinetics of the deposition of selected acrylate monomers by polymerization into chrome-tanned cattle hide. *J. Appl. Polym. Sci.* **25**, 2755–2776 (1980)
35. Santana, T.J.M., Torres, A.C., Lucero, A.M.: Extrusion and mechanical characterization of PVC-leather fiber composites. *Polym. Compos.* **19**, 431–439 (1998)
36. Santana, T.J.M., Vega, M.J.A., Lucero, A.M., Moreno, F.V.: Production of leather-like composites using chemically modified short leather fibers. I: Chemical modification by emulsion polymerization. *Polym. Compos.* **23**, 49–60 (2002)
37. Ramaraj, B.: Mechanical and thermal properties of ABS and leather waste composites. *J. Appl. Polym. Sci.* **101**, 3062–3066 (2006)
38. Santana, T.J.M., Vega, M.J.A., Marquez, A., Moreno, F.V., Richardson, M.O.W., Machin, J.L.C.: Production of leather-like composites using short leather fibers. II. Mechanical characterization. *Polym. Compos.* **23**, 991–1002 (2002)
39. Andreopoulos, A.G., Tarantili, P.A.: Waste leather particles as a filler for poly(vinyl chloride) plastisols. *J. Maromol. Sci. Part A Pure Appl. Chem.* **37**, 1353–1362 (2000)
40. Babanas, K., Tarantili, P.A., Andreopoulos, A.G.: Plasticized poly (vinyl chloride) filled with waste leather particles. *J. Elastomeres Plast.* **33**, 72–85 (2001)
41. Chronska, K., Przepiorkowska, A.: Buffing dust as a filler of carboxylated butadiene-acrylonitrile rubber and butadiene-acrylonitrile rubber. *J. Hazard. Mater.* **151**, 348–355 (2008)
42. ASTM: International Annual Book of ASTM Standards, vol. 15.04. ASTM International, West Conshohocken, PA (2001)
43. IUP 36: Measurement of leather softness. *J. Soc. Leather Technol. Chem.* **84**, 377–379 (2000)
44. IS 5914: Methods of Physical Testing of Leathers. Bureau of Indian Standards, New Delhi, India (1970)
45. Koo, C.M., Ham, H.T., Choi, M.H., Kim, S.O., Chung, I.J.: Characteristics of polyvinylpyrrolidone-layered silicate nanocomposites prepared by attrition ball milling. *Polymer* **44**, 681–689 (2003)
46. Chang, M.C., Tanaka, J.: FT-IR study for hydroxyapatite/collagen nanocomposite cross-linked by glutaraldehyde. *Biomaterials* **23**, 4811–4818 (2002)