Fabrication and Characterization of Regenerated Leather Using Chrome Shavings as Raw Materials

by

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Abstract

Regenerated leather billet (semi-finished product) was prepared via hot pressing with chrome shaving and environment-friendly polymer waterborne polyurethanes (WPU) as the materials. The influence of WPU/chrome shaving ratios (w/w) on the performance of the billet was investigated by mechanical property test, dynamic thermal mechanical analysis, thermogravimetric analysis, differential scanning calorimetry and field-emission scanning electron microscopy. Furthermore, the ability of heat storage and temperature regulation was endowed for the regenerated leather by the addition of paraffin microcapsules. The results showed that a strong interface interaction could be achieved for the regenerated leather billet, which could be due to the formation of hydrogen bonds and the entanglement between WPU and leather shavings. In this way, WPU/leather shaving composites with favorable mechanical properties, thermal stability, ability of heat storage and temperature regulation were obtained.

Introduction

Leather manufacturing is a chemical process of natural biological matrix. It employs a huge quantity of water and inorganic and organic chemicals for processing and by discharges solid and liquid wastes into the environment.[1] It was reported that the tanning process generates much greater quantities of by-products and wastes than leather.[2] About 30% of leather wastes are processed in tanneries, mainly after shaving process, in the form of protein wastes.[3] As is known, worldwide chromium-based tanning process is predominantly followed due to the versatility of chromium,[4,5] and thus the disposal of the main solid waste, chrome-tanned leather shaving (CTLS), is increasingly becoming a serious environmental challenge to leather industry due to the presence of heavy metal chromium.[6,7]

CTLSs are small, thin pieces of leather formed during shaving operation, which is being done to achieve the desired thickness for various end uses of the leather. It accounts for 15-30% of total proteinous waste generated from tannery.[8] CLTS is a chromium cross-linked protein that contains higher amount of collagen and the chromium oxide content in CLTS is about 4.4%.[9] Large quantities of CTLSs are disposed by landfill in many parts of the world, which faces the highest cost, explained by the combination of the overall high pollution emissions and low energy recovery.[10,11] Meanwhile the pressure over landfilling of wastes with high organic content and toxic substances is continuously increasing. Hence, finding a sustainable solution to the CTLS disposal problem is a primary challenge for tanners and researchers.

Many research studies have been carried out to investigate safe disposal, recovery of chromium and protein, and their reuse in various fields of industry. There are kinds of treatment methods that could be broadly classified into (I) recovery of chromium and protein from CLTS,[12,13] (II) direct use.[14,15] For the first class, the popular trend of utilization of wastes is to recover chrome(III) compounds and processing the recovered collagen into gelatin, adhesive, or protein hydrolysate. The recovered gelatin can be used in cosmetics, printing inks, and photography, and the protein hydrolysate due to its high-nitrogen content can be possibly used as fertilizer or additive to fodders, whereas the recovered chrome can be used in tanning process.[11,16,17] With respect to the direct use of chrome-tanned leather shaving, there have been many ways such as the manufacture of regenerated leathers, leather boards, fibrous sheets, filler for nitrile and butadiene–acrylonitrile rubbers, building materials after reacting with polyisocyanates.[18-20] The direct application could be an ideal way to dispose CTLSs in the energy-saving and environment-benign perspective. However, it was known that collagen fibers as the main component of CTLSs possessed poor mechanical properties, which significantly restricted the potential application of CTLSs in field of leather manufacture. Fortunately, blending natural and synthetic polymers is always an efficient and practical approach to confer the mechanical characteristic of natural polymers.[21,22]

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Manuscript received October 21, 2016, accepted for publication January 2, 2017.

Amongst all the synthetic polymers, polyurethane (PU) is one of the most important and versatile polymers. It is obtained by the rearrangement reaction between di/polyisocyanates and di/polyolcompounds.[23] The promising feature of PU is that its properties can be tailor-made by varying its compositions, structures of raw materials and NCO/OH ratio.[24] There are two types of polyurethane dispersions, namely solvent-borne and waterborne, the waterborne ones are particularly attractive due to their higher durability, better environment-friendliness and better tailoring capabilities. Waterborne polyurethane (WPU) is a widely used versatile class of material for applications in foams, coatings, adhesives, and elastomers.[25,26] Although the effects of protein-coated PU, in particular collagen have been previously investigated, there are only a handful of studies examining the properties of PU/leather shavings.[27] Addie *et al.* prepared a reconstituted leather product via blending short collagen fibers (not longer than one inch) with synthetic fibers, a resin and optionally other additives, forming the mixture into a mat, curing the mat and pressing the mat into a reconstituted leather product.[28] Lv *et al.* prepared a polyurethane membrane blended with chrome-containing leather waste. The hygienic performance and mechanical properties of collagen fiber/polyurethane complex membrane were improved.[29] However, the interactions and mechanical properties of CTLSs blended with WPU have not been investigated. It was known that the collagen fibers were positively charged after the carbonyl groups of collagen molecules are occupied by Cr (III), so the cationic polyurethane was selected to ensure that the polyurethane molecules could be well permeated into the collagen fibers of CTLSs.

Therefore, the aim of this study was to prepare the regenerated leather with chrome-tanned leather shavings and waterborne polyurethane as raw materials, and examine the mechanical properties and thermal stability of the prepared regenerated leather. Meanwhile, the interactions between collagen fibers and PU were explored. Furthermore, a new-type regenerated leather with a function of heat storage and temperature regulation was also prepared by dispersing microcapsule containing paraffin into the composites of polyurethane with leather shavings. It is hypothesized that mixing waterborne polyurethane and collagen fibers will confer high performance such as tensile strength and thermal properties to the regenerated leather.

Materials and Methods

Materials

Wet blue chrome shavings were provided by Xingning Leather Company (Jiangsu, China). The length of leather shaving fibers was roughly in the range of 2-6 mm. Cationic waterborne polyurethane (Poly[4,40-methylenebis(phenyl isocyanate)-alt-1,4-butanediol/polytetrahydrofuran]) was provided by Dymatic Chemicals (Guangdong, China). Paraffin microcapsule was purchased from Haas Chemical Company (Jiangsu, China).

Sample Preparation

Cationic waterborne polyurethane (WPU) was mixed fully with these chrome-tanned leather shavings (CTLS) in different weight ratios of 0.5/1, 1/1, 1.5/1, 2/1 and 3/1 (WPU/CTLS). Meanwhile, water was added proportionally to keep the final total weight of every mixed sample equal. The composites are denoted as PULS(0.5), PULS(1), PULS(1.5), PULS(2), PULS(2.5), and PULS(3), respectively, according to the weight ratios of WPU/CTLS. Furthermore, the microcapsule containing paraffin was added into the composite of PULS(1). The final weight percentage of paraffin microcapsule was 0%, 2.5%, 5%, 7.5%, 10% and 15%, respectively. And these samples are named as MPULS(0%), MPULS(2.5%), MPULS(5%), MPULS(7.5%), MPULS(10%) and MPULS(15%), correspondingly.

Then each of the aforementioned samples was put into the mold (a square steel slice with a hollow circle, the diameter and thickness of which are 120 mm and 0.5 mm, respectively) and was first pressed by a hot press machine at 100°C under pressure of 12 MPa for 3 min, followed by a press treatment at room temperature for 2 min. Thus, regenerated leathers with and without paraffin microcapsules were made into a round pie shape with a diameter of 120 mm and a thickness of 0.5 mm. Finally, all samples were stored at constant temperature and relative humidity system for the following experiments.

Mechanical Properties Tests of Regenerated Leathers

The tensile strength and elongation at break of the regenerated leathers were measured using the universal material testing machine (UTM 6203, China) according to standard QB/T 3812.5-1999 on 5 specimens. Each test specimen was cut into 50 mm×10 mm strips. The thickness of the regenerated leathers was measured under a pressure of 500 Pa. The testing strip was mounted to clamps of the machine with a 300 N load-cell. The gauge length used was 25 mm and the cross-head speed was set at 100 mm/min during the tests. Maximum tensile strength is the largest stress that a material is able to sustain, and ultimate elongation is the maximum percentage change in the length of a material before breaking. Each reported value was an average of five measurements.

Dynamic Mechanical Analysis (DMA)

The dynamic thermal mechanical property evaluation was carried out with a DMA (Netzsch DMA 242E, Germany), in the tensile mode, and by heating from -120 to 200°C at a rate of 10°C/min under a nitrogen atmosphere. The films with dimensions of about 5×10×0.5 mm were subjected to sinusoidal deformation with an amplitude of 10 μm.

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis of the regenerated leathers was conducted using a thermal analyzer (Netzsch TG 209; Germany). Samples (~2.5 mg) were heated from 30 to 700°C under a nitrogen atmosphere at a heating rate of 10°C/min.

Field-emission Scanning Electron Microscopy (FESEM)
The regenerated leather underwent the brittle fracture at low temperature provided by liquid nitrogen. The cross-section morphologies of the regenerated leather samples were observed via a field-emission scanning electron microscope with the accelerating voltage of 15 kV (Navo FEI NanoSEM 230, USA).

Differential Scanning Calorimetry (DSC)
The thermal behavior of the regenerated leather samples was recorded on a differential scanning calorimeter (Netzsch DSC 200PC, Germany). The samples (~2 mg) were sealed in aluminum pans and scanned over the range from 10 to 150°C at a heating rate of 10°C/min in a nitrogen atmosphere. Liquid nitrogen was used as a cooling medium and empty pans were used as the reference.

Results and Discussion

Mechanical Properties of Regenerated Leathers
The blends were heterogeneous when the leather shavings were mixed with WPU solution at room temperature. WPU wetted and permeated the collagen fibers but not formed interactions. The blends were laid in a steel mold and undergone the hot-press process. As the evaporation of water, there were irreversible contact between the emulsion particles and then these emulsion particles tended to arrange regularly.[27] Collagen fibers passed through the interfaces of emulsion particles and coagulated, which brought about the appearance of the interfaces of emulsion particles and the formation of the regenerated leather billet. The digital photographic images of the prepared regenerated leather billets are shown in Figure 1.

Tensile strength and elongation at break of the regenerated leathers with WPU/LS ratios of 0.5/1, 1/1, 1.5/1, 2/1, 2.5/1 and 3/1 are shown in Figure 2. Figure 2(a) shows that the tensile strength values of the regenerated leathers were firstly increased with the ratio of WPU/LS increased to 2/1, while it decreased as WPU content increased, which indicated that the strength or pattern of the interactions between collagen fibers and WPU were possibly varied. As can be seen from Figure 2(b), the breaking elongation was monotonically increased as the WPU content increased. This revealed that chrome-tanned collagen fibers distributed in the inside of WPU network, could limit the elongation freedom of WPU.

Figure 2(c) and Figure 2(d) present the tensile strength and elongation at break of the regenerated leather with paraffin microcapsule contents of 0, 2.5, 5, 7.5, 10 and 15%. As can be seen, the tensile strength of regenerated leather showed a tendency to decline with the adding amount of paraffin microcapsules, probably owing to the "isolation effect" of microcapsules on the interactions between collagen fibers and WPU molecules. However, the breaking elongation of regenerated leather was slightly improved with small amount of paraffin microcapsule contents (<7.5%), mainly because the "isolation effect" of paraffin microcapsules weakened the interactions among molecules, leading to the flexibility of molecular chain increased. While the breaking elongation of regenerated leather significantly decreased with the paraffin microcapsule contents further increased, which was probably due to the excessively strong "isolation effect" of microcapsules on the interface interactions made some tiny cracks formed in the regenerated leather billet.

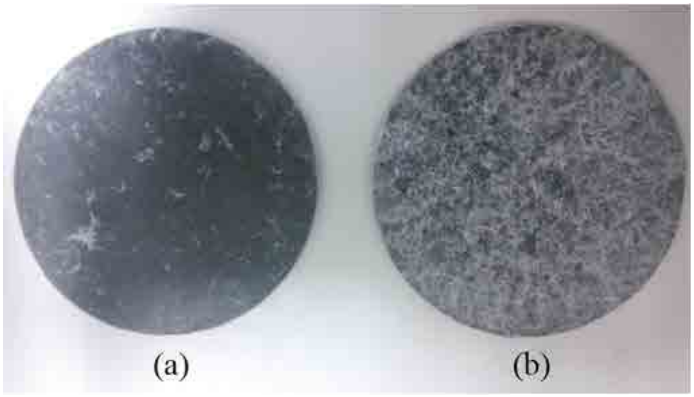

Figure 1. Digital photographic images of the prepared regenerated leather billets. Sample with paraffin microcapsules (a); Sample without paraffin microcapsules (b).

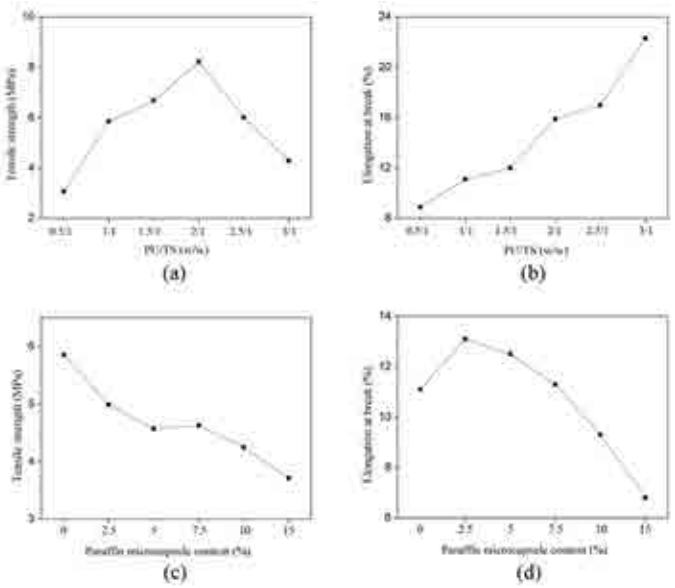

Figure 2. Tensile strength and elongation at break of the regenerated leathers with PU/LS ratios of 0.5/1, 1/1, 1.5/1, 2/1, 2.5/1 and 3/1 (a, b); Tensile strength and elongation at break of regenerated leather with paraffin microcapsule contents of 0, 2.5, 5, 7.5, 10 and 15% (c, d).

Dynamic Thermal Mechanical Properties of Regenerated Leathers

Dynamic mechanical analysis (DMA) experiments were conducted to measure the thermo mechanical strength of the regenerated leathers by monitoring temperature-modulus curves. Figure 3(a) and Figure 3(b) respectively show the tanδ (ratio of loss modulus to storage modulus) curves of the regenerated leathers with different WPU/LS ratios and with different paraffin microcapsule contents, as a function of temperature in the range of -120 to 200°C. The corresponding peaks of tanδ are listed in Table I and Table II.

It could be seen from Figure 3(a) that, as for all samples, the maximum tanδ values of collagen fibers were at approximately 130°C, generally consistent with the results of Witnauer and Fee[31] as well as Flory and Garrett.[32] They reported the melting point of collagen was about 145°C and no glass transition temperature could be detected before appreciable thermal degradation took place. Different from the collagen fibers, the thermogram of WPU exhibited two peaks assigned to soft segments and hard segments. The first peak at about -50°C, designated as the relaxation, represents the glass transition temperature (T_g) of WPU. The second peak located at approximately 50°C was due to the relaxation in the WPU crystalline domains. The values of T_g were basically in accordance with the results in other literatures.[33,34]

From Table I, it could be found that the T_g of soft segments of WPU was hardly influenced by collagen fibers. While the relaxation peak of the hard segments in the crystalline domains firstly shifted to the lower temperature till the ratio of WPU/LS reached 2/1, indicating the degree of micro crystal in

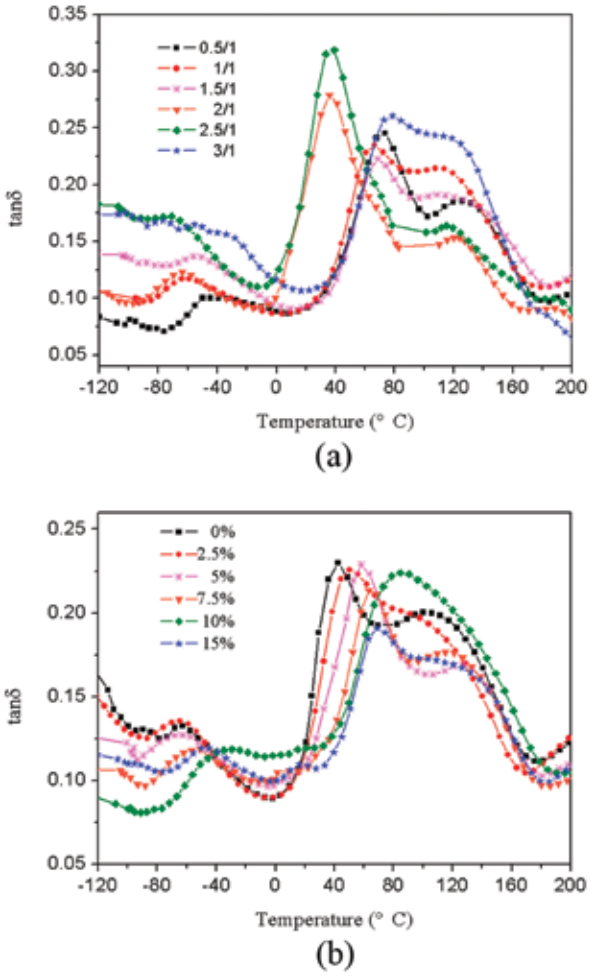

Figure 3. Loss factor (tanδ) of regenerated leathers with WPU/LS ratios of 0.5/1, 1/1, 1.5/1, 2/1, 2.5/1 and 3/1(a); tanδ of regenerated leather with paraffin microcapsule contents of 0, 2.5, 5, 7.5, 10 and 15% (b) measured by dynamic mechanical analysis (scanning rate: 10 K min^{-1}; 5 Hz).

Table I

Values of Tg in dynamic mechanical analysis of samples with different WPU/LS ratios.

	0.5/1	1/1	1.5/1	2/1	2.5/1	3/1
Tg of soft segments (°C)	-39.162	-64.105	-56.221	-63.906	-71.067	-55.551
Tg of hard segments (°C)	73.557	66.176	68.557	35.773	39.182	78.582

Table II

Values of Tg in dynamic mechanical analysis of samples with different microcapsule contents.

	0%	2.5%	5%	7.5%	10%	15%
Tg of soft segments (°C)	-62.986	-64.606	-62.885	-50.777	-29.4	-44.762
Tg of hard segments (°C)	42.571	50.287	58.74	63.696	84.633	98.837

the molecules of WPU decreased, which can be explained as follows. In the composites of WPU and collagen fibers, the hydrogen bonding formed between the amino groups of WPU and hydroxyl or amino groups of collagen, plus the molecular entanglement among WPU and collagen fibers attenuated the degree of micro crystal in WPU molecules, hence the glass transition temperature was decreased. Interestingly, the relaxation peak values of hard segments of WPU increased sharply as the ratios of WPU/LS kept increasing, which revealed that the degree of micro crystal in WPU molecules was not obviously influenced by the interactions of collagen fibers and WPU molecules.

Combining with the Figure 3(b) and Table II, it could be found that the T_g of all soft segments and hard segments of WPU in regenerated leather was shifted to higher temperature with paraffin microcapsule contents increased, which was probably due to that the movement of the chain segments had space obstacle owing to the filling effect of microcapsules.

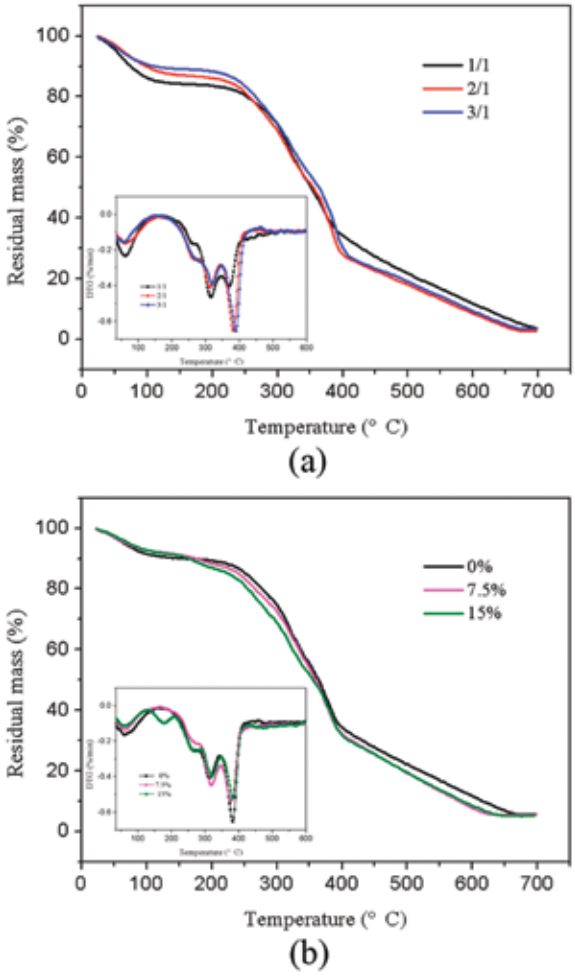

Figure 4. Thermogravimetric curves of regenerated leathers of WPU/LS(a) and MPULS(b) obtained at a heating rate of 10°C/min under a dynamic N_2 atmosphere (DTG curves at bottom left).

Thermogravimetric Analysis of Regenerated Leathers

The thermal gravimetric curves of regenerated leathers are presented in Figure 4. The derivative thermogravimetric (DTG) curves at the bottom left show the temperature of decomposition with a maximum speed (T_{m1} and T_{m2}), which are listed in Table III and Table IV. It was clear that there were three degradation stages. The first stage represents evaporation of unbound water. The second stage is dehydration and volatilization of low-molecular weight substances and the third stage is the main degradation stage.[35]

From Table III, it could be seen that there was hardly any difference in the second thermal event at about 315°C (T_{m1}). With respect to the main degradation stage, the thermal decomposition of WPU/LS (2/1) and WPU/LS (3/1) samples was occurred at a higher temperature than that of WPU/LS (1/1), indicating the regenerated leather possessed a higher stability toward thermal degradation as WPU/LS ratio was no less than 2/1. In addition, as shown in Table IV, the addition of paraffin microcapsules had little influence on the degradation profile for the composites of collagen fibers and WPU.

Morphology of Regenerated Leathers

Figure 5 shows the cross-section morphologies of regenerated leathers with different ratios of WPU/LS (Figure 5a, Figure 5b and Figure 5c) and regenerated leathers containing different content of paraffin microcapsules (Figure 5a1, Figure 5b1 and Figure 5c1). As can be seen, there was a good adhesion at the

Table III
Values of temperature of decomposition with a maximum speed (T_{m1} and T_{m2}) of samples with different WPU/LS ratios.

	1/1	2/1	3/1
T_{m1} (°C)	315.4	312.8	315.3
T_{m2} (°C)	367.8	382.8	390.3

Table IV
Values of temperature of decomposition with a maximum speed (T_{m1} and T_{m2}) of samples with different content of microcapsules.

	0%	7.5%	15%
T_{m1} (°C)	320.5	320.5	322.9
T_{m2} (°C)	375.4	375.5	385.4

interface between collagen fibers and PU, resulting from the entanglement effect and hydrogen bonding interactions between collagen and PU molecules. For sample WPU/LS(1/1), it could be seen that a large amount of collagen fibers were stacked and entangled themselves, and obviously this kind of stack and entanglement effects was not enough to construct a strong network (Figure 5a). As the WPU content increased, there were networks well-structured by PU molecules and the entangled collagen fibers were wrapped in there, thus forming high-performance regenerated leathers (Figure 5b). While the WPU content was further increased (Figure 5c), some entangled collagen fibers were forced to be separated, which probably lowered the cohesion of the whole structure of regenerated leathers.

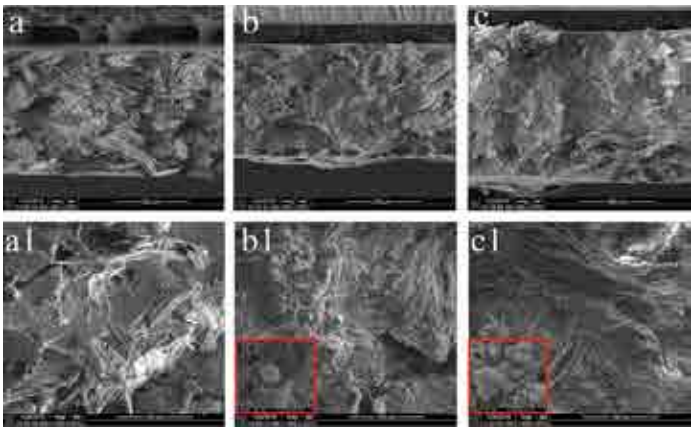

Figure 5. SEM cross-sections of regenerated leathers of WPU/LS(1/1) (a), WPU/LS(2/1) (b) and WPU/LS(3/1) (c) with a magnification of 200. Bars, 500 μm; cross-sections of samples with paraffin microcapsule contents of MPULS(0%) (a1), MPULS(7.5%) (b1), and MPULS(15%) (c1) with a magnification of 1000. Bars, 100 μm. Small figures at bottom left (b1 and c1) with a magnification of 5000 (the red outline).

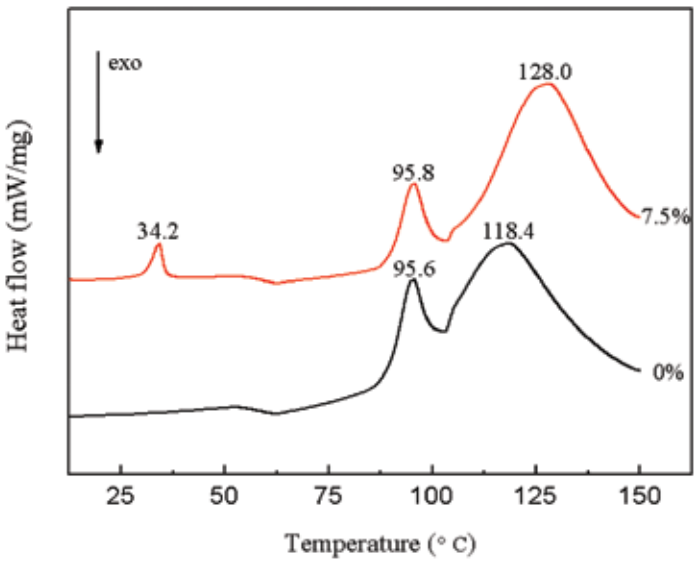

Figure 6. Differential scanning calorimetry curves for regenerated leathers with and without paraffin microcapsules.

Figure 5a1, Figure 5b1 and Figure 5c1 show the effect of paraffin microcapsule contents on its dispersion morphology in the regenerated leather matrix. As can be seen, both the microcapsules in different content (7.5% and 15%) were well dispersed in the regenerated leathers. When making a comparison of MPULS(7.5%) with MPULS(15%), it could be found that the microcapsules with larger content were easily dispersed between collagen fibers (Figure 5b1 and Figure 5c1), which caused mechanical properties of regenerated leathers reduced. In addition, the shape of microcapsules in regenerated leather matrix remained intact as presented in small figures at bottom left (Figure 5b1 and Figure 5c1), indicating that a kind of regenerated leather with effect of heat storage and temperature regulation was obtained.

DSC Thermograms of Regenerated Leathers

Thermal properties of regenerated leathers with and without paraffin microcapsules are presented in Figure 6. It could be found that the regenerated leather sample without paraffin microcapsule exhibited two endothermic peak at 95.6 and 118.4°C, while there were peaks at about 34°C for sample containing paraffin microcapsules, resulting from the endothermic process of the phase transition of paraffin.[36] Again, the phase transition peak of paraffin revealed that paraffin microcapsules were dispersed in the regenerated leathers (as confirmed by FESEM). So when the ambient temperature was higher than the phase transition temperature, the paraffin microcapsules dispersed in the regenerated leathers would change phase and absorb heat, and thus decreased the ambient temperature and made people feel comfortable. Similarly, the effect heat preservation of paraffin microcapsules works in adverse as the ambient temperature was lower than the phase transition temperature.

It should be noted that, for sample MPULS(7.5%), the melting peak shift to higher temperature region (128.0°C), which was well consistent with the results of DMA. This might attribute to the preventing of microcapsule from heat transfer process of collagen fibers.[37]

Conclusions

The recycling of chrome-containing leather shavings is of great importance and a huge challenge. The present paper reported a simple but effective recycle technology of chrome-containing leather shavings by mixing with waterborne polyurethane and successfully obtained regenerated leather billet. The experimental results showed that the waterborne polyurethane/leather shaving composites with good performances, for example, high tensile strength, thermal stability, and heat-storage ability, were obtained. Compared with the conventional chemical methods of recycling leather shavings, the technology

reported in this paper saved the resources and did not produce the secondary pollution such as the waste water. Therefore, it can be a convenient, cost-efficient and environment-friendly technology to deal with the problem of recycling the chrome-containing leather shavings.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (Grant No. 21606046 and Grant No. 21306024), the Natural Science Foundation of Fujian Province (Grant No. 2016J01208) and the General project of Fujian Provincial Department of Education (Grant No. JA15344).

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