EFFECTS OF CHOLINE CHLORIDE, UREA AND THEIR DEEP EUTECTIC SOLVENTS ON THE MODIFICATION OF LEATHER

Letian Qi[1,a)], Lihong Fu[2]

1 State Key Laboratory of Biobased Material and Green Papermaking, Qilu University of Technology, Shandong Academy of Sciences, Jinan, 250353.

2 School of Light Industry Science and Engineering, Qilu University of Technology, Shandong Academy of Sciences, Jinan, 250353.

a)Corresponding author: lqi01@qlu.edu.cn

Abstract. The application of split leather is an important issue in leather industry as most of them was not properly treated and wasted. In this study the application of choline chloride ([Ch][Cl]), urea (U) and corresponding deep eutectic solvents (DES) on the modification of thermal stability and mechanical strength of mink split leather was investigated. TGA and DSC results indicated DES treatment enhanced thermal stability of split leather, and [Ch][Cl] treatment reduced the stability. While, U treatment provided a kinetic inhibition during the thermal-decomposition. In terms of the mechanical strength, both [Ch][Cl] and U treatment reduced burst intensity and extended height. While, after DES treatment the burst intensity and extended height increased significantly. In terms of the dosage, 7% DES provided best performance. Results mentioned above illustrated that DES formed by simply mixing [Ch][Cl] and U provided strong interaction with fiber, enhanced the crosslinks. A hypothesis of [Ch(Urea)]+[Cl(Urea)]- type structure was proposed, as it enabled DES forming strong hydrogen bonds with functional groups on leather fiber, enhancing the crosslinks and therefore improving the thermal stability and mechanical strength. The DES treatment on leather fibers improved their overall performance and thereby broaden their applications.

1 Background

The split leather is an important leather and bio-based material in tanning industry, whose physical properties can be improved to expand applications. However, it was not properly treated during the tanning process and a great portion was wasted. For example, split mink leather was discarded during the shaving process, for its small area, low physical strength and poor thermal stability. This caused the waste of high-quality collagen materials and a pollution to the environment.

The utilization of split leather requires thermal treatment either directly or after a chemical pretreatment to improve the physical strength. In which, thermo-treatment was commonly used in the direct processing. However, the poor thermal stability and extensibility prohibit the application of mink split leather. In addition, the thermal decomposition and denature of collagen also cause problem during the utilizations. Retanning and ester addition are the most widely used chemical treatments, which improve the leather performance, thereby broad its applications. Chrome tanning is the most commonly used tanning technic, which enhances the crosslink between collagen fibers. As the crosslink directly related to the thermal stability and physical strength, chrome tanning helps improving the thermal and physical properties of the leather. However, the major concern is environmental pollutions induced by chrome containing chemicals. Fat liquoring agent improves the softness of leather but decreases the physical strength of leather. The other draw back includes the large dosage and poor biodegradability, which causes problems in the downstream processes. Thereby, both academic and industrial side focused on developing a greener, environmental-friendly approach to enhance the physical strength and thermal stability of the leather.

Ionic liquids (IL) are nova green solvents with merits of good solubility, nonvolatile, easy to recycle, low toxicity, environment friendly, and tunable. Therefore, it was extensively studied in chemistry, chemical engineering, material, biology field. The strong electronic effect and H-bonding

was found in ionic liquids, thereby it is ideal to improve the physical strength of leather. Jayakumar et al.[1] firstly reported that [BMIM][Cl] ionic liquid loosed the leather fibers, pointing out the potential of apply IL in dehairing process. Latterly, Alla et al.[2] successfully applied [BMIM][BF_4] ionic liquid in the dehairing and fiber loosing process. In addition, Ranganathan et al.[3] reported that quaternary ammonium based ionic liquids could disturb the disulfide bond in keratin/certain, cause the dehair effect and improve the physical strength of leather. However, the study of IL application on tanning process are still limited to the commercial availability of ILs, which are usually expensive and prevented their further applications.

Choline based ionic liquids are generally cheap and environment friendly. Therefore, it is an ideal bio-based material treatment agent. It contains multiple H-bonding sites such as halogen anions and hydroxide groups on cations, which act as H-bond acceptors and donors, respectively. These H-bonding sites could interact with functional groups on collagen fibers, forming multiple H-bonds. At the main time, as an ampholyte the leather fiber also interacts with IL cations and anions through coulomb force. Thereby, the application of choline based ILs should be able to improve the crosslinks of the collagen fibers, resulting in an enhancement of leather physical strength and thermal stability. On the other hand, urea (U) is an important additive in leather industry, which was usually used in liming treatment process[4]. Urea molecule interacts with collagen fibers through H-bonds on amino and carbonyl groups. Therefore, it could disturb the collagen-water interactions in leather and modify the leather properties [5].

Mix [Ch][Cl] with urea at 1:2 molar ratio generates deep eutectic solvent (DES) with melting point as low as 12 ℃. In comparison, the melting point of [Ch][Cl] and urea under atmosphere pressure are 300 and 133 ℃, respectively. The decrease of melting point indicates the present of strong H-bonds. Liquid state also makes pumping and injecting more continent to achieve in process. Therefore, [Ch][Cl]-U DES is an ideal leather fiber treatment agent, as it may provide dual function from both [Ch][Cl] and urea side and may also present some new features. Abbott et al.[6] reported that DES present high electronic interactions that makes tanning agent much easier getting into leathers. Thereby, the application of DES based ionic liquids can be used to replace traditional solvent. This work was the first to ingratiate the application of DES on mink split leather. [Ch][Cl]-U (A), [Ch][Cl] (A0), and urea (U) was applied for mink split leather treatment, in order to study their effect on physical strength and thermal stability. The study provides important information over the mechanism of DES-collagen fiber interactions.

2 Experimental

2.1 Materials

Mink split leather was obtained from a leather company in Shandong Province, P. R. China. Chemicals used for leather treatment and DES synthesis, including source and grade, were as following:

Choline chloride (AR, 98-101%, Sinopharm Chemical Reagent Co., Ltd.), urea (AR, 99.0%, Tianjin Da Mao Chemical Co.). [Ch][Cl]-U DES was synthesized by mixing choline chloride and urea at 1:2 molar ratio under 60 ℃ for 4 hr. Ultra-pure water (18 MΩ·cm) was supplied by JNLC Water Purification System, P. R. China.

2.2 Chemical Treatment on Mink Leather

The mink split leather was washed and squeeze-dried 3 times with ultra-pure water, followed by stabilizing in polyethylene bag for 30 min (water content 55.95%). Then, water ($w_{wet\ leather}$: $w_{water} = 1:10$) was added into stabilized leather samples, with or without the

addition of treatment chemicals. Chemicals were added basing on the dry weight of leather, and 5 different treatment conditions were listed as following:

0% (blank test), 7%[Ch][Cl]-U, 14% [Ch][Cl]-Cl, 7% [Ch][Cl] and 7% U.

Treatment was carried out under room temperature (19 ℃) for 37.5 hr, ceased by removing leather samples from the aqueous solutions. The samples were air-dried for 24 hr, prior thermal analysis and physical strength tests.

2.3 Thermal Analysis

Thermal characterization of treated and untreated leather samples included thermal gravimetric (TG), differential thermal gravimetric (DTG) and differential scanning calorimeter (DSC) techniques.

TG/DTG analysis was performed using TGA-Q50 apparatus, produced by TA Instruments, US, in N_2 atmosphere and 20-500 ℃ temperature range, at a heating rate of 5 $℃/\mathrm{min}$.

DSC analysis was performed using DSC-Q20 apparatus, produced by TA Instrument, US, in N_2 atmosphere and 30-350 ℃ temperature range, at a heating rate of 10 $℃/\mathrm{min}$. Samples weighted 5–6 mg was placed in aluminium pan to perform the test.

2.4 Mechanical Strength Analysis

Air-dried leather samples were conditioned at 20 ℃, RH 65% for 24 hr, in a YG751D constant temperature and humidity incubator, produced by Shanghai Jing Hong Laboratory Instrument Co., Ltd. Burst intensity and extended height was analysed by XK-3055 burst intensity tester, produced by Xiangke Testing Instrument Co., Ltd. Following equations were used during the determinations of the mechanical strengths:

$$\text{Burst intensity} = \mathrm{F}/\delta \tag{1}$$

$$\text{Extended height} = \mathrm{h} \tag{2}$$

Where, F is the load at fracture (N), h is the extended height at fracture (mm), δ is the thickness of testing samples (mm).

3 Results and Discussions

3.1. Thermal Gravimetric Analysis (TGA)

Thermal gravimetric analysis of leather samples treated by different chemicals were illustrated in Fig.1 (a). All the samples viewed a 5% weight loss between 30 to 125 ℃, followed by sharp drop from 250 ℃. Leather pretreated by [Ch][Cl]-U presented TG curve of the same trend but above the blank test, thereby its thermal stability was slightly better than the blank test. TG curve of 7% A0 is lower than blank test, thereby this treatment reduced the thermal stability of the leather sample. However, the 7% U treatment results moved towards the upper right corner, indicating an enhancement in thermal stability.

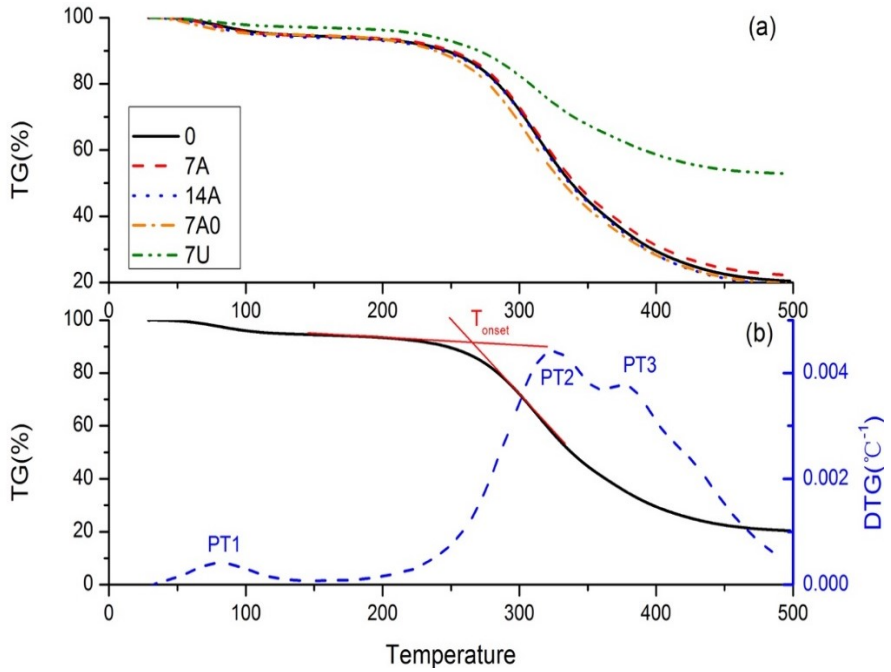

Fig. 1. Thermal gravimetric (a) and differential thermal gravimetric (b) of mink spilt leather. Note: 0, blank test; 7 A, 7% [Ch][Cl]-U; 14 A, 14% [Ch][Cl]-U; 7 A0, 7% [Ch][Cl]; 7 U, 7% urea.

Differential thermal gravimetric analysis provided more detailed information. Taking the blank test data in Fig. 1 (b) for example, the mass change of leather sample under N_2 environment could be classified into 2 stages: the first stage is dehydration of leather sample, which was shown as peak PT1 at 82 ℃; the second stage was the thermal decomposition of collagen, which was PT2, PT3 at 325 and 376 ℃, respectively. T_{onset} can be considered as the cut-off point of the two stages mentioned above. Details of TG, DTG analysis can be found in Table 1.

Table 1. Effect of different treatment on the thermal stability of mink split leather.

	0%		7% [Ch][Cl]-U		14% [Ch][Cl]-U		7% [Ch][Cl]		7% U	
	T (℃)	Weight loss (%)	T (℃)	Weight loss (%)	T (℃)	Weight loss (%)	T (℃)	Weight loss (%)	T (℃)	Weight loss (%)
PT1	82.3	2.5	77.9	2.5	78.7	2.9	65.2	2.3	77.5	1.3
T_{onset}	265.0	7.3	267.0	6.8	266.8	7.4	257.6	7.7	257.7	4.3
PT2	325.2	43.2	325.0	41.8	321.1	41.5	316.0	41.5	315.0	22.5
PT3	375.8	64.2	378.6	63.2	380.2	66.3	370.7	64.4	379.1	38.0

As shown in Table 1, the IL treatment shifted the appearance of dehydration peak (PT1), and all of which were lower than the normal boiling point of water (100 ℃). Thereby, the mass loss at PT1 could attribute to the removal of free water. PT1 of blank sample occurred at 82.26 ℃, and the treated samples moved towards lower temperature, where PT1 of 7% and 14% [Ch][Cl]-U occurred at 78 ℃, the 7% [Ch][Cl] peak occurred at 65 ℃. Under the same dosage (7 wt% loading) the PT1 appearance temperature from high to low was: $[\mathrm{Ch}][\mathrm{Cl}] - \mathrm{U} \geq \mathrm{U} \gg [\mathrm{Ch}][\mathrm{Cl}]$ Which indicates the various effect of leather fiber holding onto water molecular. It should be noticed that, although 7% U presented similar dehydration temperature with 7% [Ch][Cl]-U, its weight loss was much lower. The shift of PT1 towards lower temperature after chemical treatment could attribute to the formation of hydrogen bond and electronic interactions between chemicals and collagen fibers.

These interactions occupied the H-bonding sites for water-fiber interactions, thereby reduced the overall fiber-water interactions through its functional groups. This phenomenon caused the increase of water activity, leading to an easier removal of water molecule, thereby moved the PT1 peak towards lower temperatures. To this point, the dehydration temperature illustrated the strength of interaction between the collagen fiber and treatment agent. The PT1 temperature of treated sample from high to low ranked:$7\%\ [\mathrm{Ch}][\mathrm{Cl}] \ll 7\%\ \mathrm{U} \leq 7\%\ [\mathrm{Ch}][\mathrm{Cl}] - \mathrm{U} < 14\%\ [\mathrm{Ch}][\mathrm{Cl}] - \mathrm{U} < 0\%$. These results indicate that A0 could from stronger interactions than A and U.

T_{onset} was the temperature that samples started thermal decompositions, which represented the thermal stability of leather. The T_{onset} of blank test was 265.0 °C, samples treated by 7% and 14% [Ch][Cl]-U were having T_{onset} of 267 °C, while 7% [Ch][Cl] and U treatment reduced the T_{onset} to 258 °C. 7% U treatment gives leather a different thermal performance, as only 4.3% weight loss was observed. In comparison, the 7% [Ch][Cl] and [Ch][Cl]-U treatment lost 7.7% and 6.8%, respectively. In addition, with the increase of the dosage of [Ch][Cl]-U from 7% to 14 %, the weight loss increased from 6.8% to 7.4%. These results indicated that the treatment chemicals applied in this research presented different effect: [Ch][Cl]-U treatment improved the crosslinks between fibers, thereby improved the thermal stability; [Ch][Cl] interacted with collagen fiber but formed limited crosslinks with fibers due to its small size, resulting in a decrease in thermal stability, and achieved a high thermal decomposition ratio; U treatment failed to bring up the T_{onset} of the leather, however, delayed the decomposition process. The ratio of leather samples decomposed was only half of the amount in other samples. Therefore, it presented more a kinetic inhibition effect. It may possibly cause by the small molecule size of urea allowing it inserted between fibers and enlarged the fiber distance, thereby inhibited the crosslink between fibers, resulted in a decrease in the thermal stability. Hereby, [Ch][Cl] and U have synergistic effect, which made [Ch][Cl]-U an efficient treatment chemical in improving thermal stabilities of leather.

PT2 and PT3 were rapid decomposition peaks. From Fig.1 and Table 1, [Ch][Cl]-U and [Ch][Cl] treatment presented similar thermal behavior with the blank test during this period, while 7% [Ch][Cl]-U treatment presented a better thermal stability. U treatment did not shift the peak position of PT2 and PT3 towards higher temperatures. However, Fig. 1 illustrated that the decomposition process in this temperature range was also significantly delayed after U treatment. The results supported the previous propose that U treatment inhibited the thermal decomposition process of collagen fibers.

3.2 Differential Scanning Calorimeter Analysis

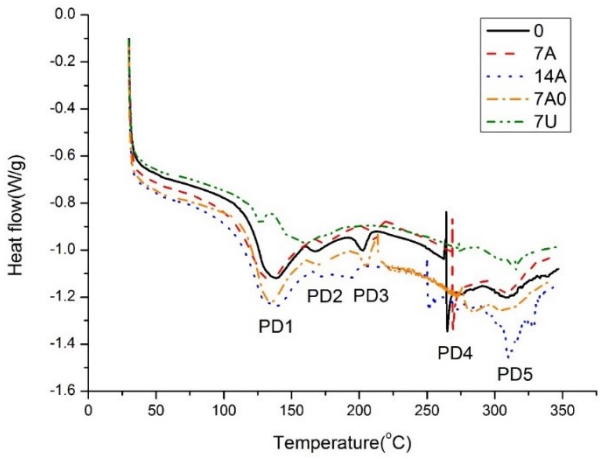

Fig. 2. Effect of different treatment on the DSC of leather with or without treatment. Note: 0, blank test; 7 A, 7% [Ch][Cl]-U; 14 A, 14% [Ch][Cl]-U; 7 A0, 7% [Ch][Cl]; 7 U, 7% urea.

Table 2. Assignment of DSC peaks of treated and untreated leather.

Peak / (°C)	Blank	7% [Ch][Cl]-U	14% [Ch][Cl]-U	7% [Ch][Cl]	7% U
PD1	138.8	134.7	139.2	135.6	127.5
PD2	167.4	173.8	172.2	169.2	161.3
PD3	202.9	212.1	194.2	205.1	NA
PD4	265.0	269.2	254.9	285.6	274.5
PD5	310.4	310.1	310.1	305.9	315.7

Previously, TGA results illustrated thermal decomposition of leather has 3 stages, which was in line with that reported by Cheng et al.[7]. Corresponding DSC results was shown in Fig. 2 and details of peak assignments was presented in Table 2, in which the first stage was the dehydration stage from 30 to 125 ℃, including PD1. The second stage from 125 to 250 ℃, including PD2 and PD3, represented the thermal behavior before the decomposition. In this stage, a melting of crystalline collagen in amorphous occurred[8], as only minor weight loss was observed. The third stage was the rapid decomposition stage from 250 to 350 ℃, including PD4 and PD5.

Thermal behavior of leather in the first stage was closely related with combined water, which played an important role while stabilizing the collagen fibers. In Fig. 2 leather samples presented a trend of an endothermic peak (PD1) followed by two small peaks (PD2, PD3), which was similar with that reported by Budrugeac et al.[9]. Therefore, the occurrence of PD1 at 135 ℃ could be attributed to the dehydration of leather, which represented the removal of bonded water. In addition, the enthalpy changes (ΔH) at PD1 was related to the strength of water molecules bonded with collagen fibers. Higher ΔH value indicated the requirement of more energy for water removal, thereby, a stronger water-fiber exists. As shown in Table 3, the ΔH value of tested leather samples from high to low ranked as:$7\%\ [Ch][Cl] \gg 7\%\ [Ch][Cl] - U > 14\%\ [Ch][Cl] - U \gg 0\% \gg 7\%\ U$.

Table 3. Effect of different treatment on the enthalpy changes (ΔH) of treated and untreated leather.

ΔH (J/g)	Blank	7% [Ch][Cl]-U	14% [Ch][Cl]-U	7% [Ch][Cl]	7% U
PD1	-32.55	-49.08	-47.58	-61.23	-3.12
PD2	-1.94	-1.78	-0.52	-2.27	-21.88
PD3	-3.20	-2.70	-1.81	-4.03	NA

Varies H-bonding sites on [Ch][Cl] allowed it to from strong interaction with water molecules, made the bonded water difficult to remove. Thus, [Ch][Cl] treatment requires the most energy for water removal. This also illustrated that only limited crosslink was caused between fibers after [Ch][Cl] treatment, as most of [Ch][Cl] molecules just remained in the fiber gaps and was not bounded with fibers. In the same manner, [Ch][Cl]-U molecule also have multiple H-bond sites, but due to the large molecular size, it can form more effective crosslinks between fibers. Thereby, a lower ΔH was required to remove water in 7% [Ch][Cl]-U treated leather sample than the [Ch][Cl] treated one. The addition of [Ch][Cl]-U resulted in an increase formation of intermolecular interactions with each other, instead of fiber crosslinks. Therefore, excess [Ch][Cl]-U enlarged the gap between fiber, which helped with the dehydration process, resulting in a decrease of ΔH value. In terms of U, it has a relatively weaker interaction with water molecules[10], thereby require less energy, leaving the dehydration process occurs at a lower temperature than other samples.

At PD2 and PD3, endothermal phenomenon occurs but no significate weight loss was viewed in TGA. This could be attribute to the rearrangement of crystalline and amorphous structure of collagen. Budrugeac[8] reported that the well-organized collagen triple helix was immersed in the

amorphous region, and the endothermal phenomenon viewed was caused by the transfer of crystalline collagen towards amorphous state. It was reported that collagen melt at 230 ℃[9], which was close to the PD3 in this work. At this temperature dry thermal shrinkage occurred[11,12], where microcosmic melting of crystalline region resulting in a macrocosmic collapse of leather matrix structure[13]. In this work, the PD2 temperature of treated samples from high to low ranked as:$7\%\ [Ch][Cl]-U > 14\%\ [Ch][Cl]-U > 7\%\ [Ch][Cl] > 0\% > 7\%\ U$. While for PD3:$7\%\ [Ch][Cl]-U > 7\%\ [Ch][Cl] > 0\% > 14\%\ [Ch][Cl]-U$. 7% U sample had no PD3. Higher PD2, PD3 value indicates better thermal stability. Thereby, 7% [Ch][Cl]-U treated sample presented highest temperature at PD2 and PD3, and presented the best thermal stability. It should be point out that U treatment, again, presented different thermal behavior than others. Although its PD2 appeared at a relative lower temperature, this peak was rather flat in comparison with other samples. Therefore, it provided more kinetic decomposition inhibition effect during the test, and this finding again supported the previous proposed mechanism.

PD4 occurs at 255-286 ℃, at which point the collagen was denatured[14]. Combining TG results analyzed previously, leather samples started thermal decomposition. DSC curve presenting a trend of sharp increase followed by a significate decrease. This may due to the rearrangement of hydrophobic bonds[13]. The cleavage of hydrophobic bonds releases energy, followed by the formation of new bonds, consume energy[13]. PD5 is the rapid thermal decomposition of leather. Interestingly, thermal behavior of U treated leather at PD4, PD5 are again different with other samples, indicating their different effect.

To summarize up, [Ch][Cl] treatment slightly decreased the thermal stability of leather, whereas, [Ch][Cl]-U generated by mixing [Ch][Cl] with U, caused crosslinks with fibers, improved the thermal stability of leather. 7% [Ch][Cl]-U treated leather presented good thermal stability, however excess application of 14% [Ch][Cl]-U, reduced the thermal stability. In terms of U, it worked as a kinetic inhibitor during the decomposition, mainly filled in the collagen fiber gaps. Although, it did not lift the thermal decomposition temperature, the decomposition rate was significantly delayed. Thereby, although [Ch][Cl]-U was synthesized by [Ch][Cl] and U, it provided both strong ionic charge center and various H-bond sites and presented very different effect than either of them. Comparing with [Ch][Cl] and U, [Ch][Cl]-U has a more suitable molecule size to form crosslinks between fibers, and to enhance the leather properties.

3.3 Mechanical Strength Analysis

Burst intensity reflected the strength of fibers in all directions and its crosslink intensities, while extended height indicated the mobility of fibers. Higher burst intensity was related to higher crosslink between fibers, and higher extended height was related to better molecule movements. It can be seen in Fig. 3, [Ch][Cl] and U treatment reduced the extended height and burst intensity, which could attribute to the small molecular size that allowing them to get into leather fibers. The enlargement of fiber gaps inhibited the formation of crosslinks between fibers and reduced the burst intensity. Applying U on its own formed multiple H-bonds with fiber, resulted in an increase in stiffness and brittleness of leather, and reduced the extended height significantly. In terms of [Ch][Cl]-U, it formed H-bonds and electrovalent bonds with leather fibers, improved fiber crosslink and enlarged the fiber distance. Therefore, [Ch][Cl]-U treatment improved extended height and burst intensity at the same time.

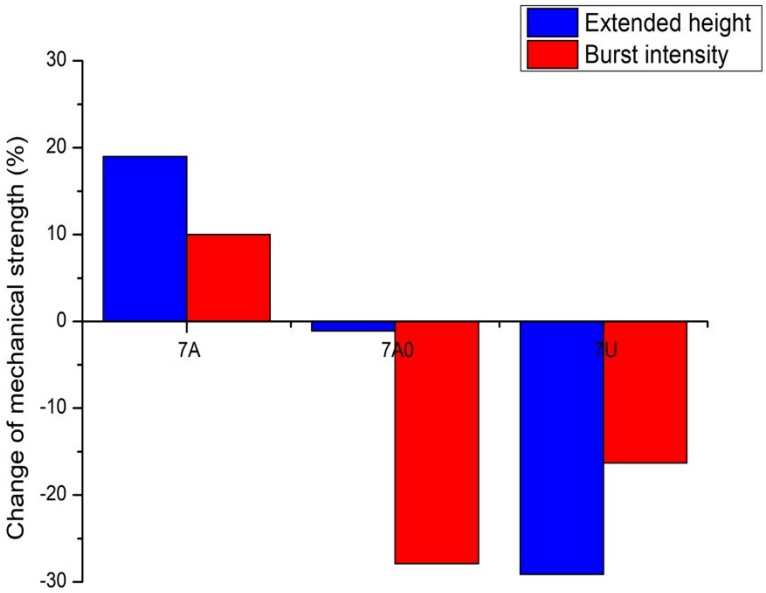

Fig. 3. Effect of different treatment on the burst intensity ang extended height of leather. Note: 7 A, 7% [Ch][Cl]-U; 14 A, 14% [Ch][Cl]-U; 7 A0, 7% [Ch][Cl]; 7 U, 7% urea.

In this work, both the physical strength test and thermal stability tests results illustrated that [Ch][Cl]-U treatment provided different effect than [Ch][Cl] and U. This should attribute to their different molecular structures: choline chloride was a quaternary ammonium-based IL, its anion had strong H-bond accepting ability. The quaternary ammonium based ILs was used for synthesizing deep eutectic solvents (DES) by simply mixed with H-bond donors, such as urea. In terms of the molecular structure, it was commonly considered that in this [Ch][Cl]-2Urea DES system, two urea molecules was complexed with chloride anion, appeared as $[Ch]^+$ $[Cl(Urea)_2]^-$ type structure[15]. However, this theory cannot well explain the phenomenon that was found in this work. The anion of [Ch][Cl] provided strong H-bond accepting ability, which was considered as main contribution of H-bonding abilities. The combination of two urea with chloride anion formed a complex anion but consumed the H-bond accepting sites on $[Cl]^-$, reduced the overall H-bond accepting ability. In terms of cation, the cation of $[Ch]^+$ $[Cl(Urea)_2]^-$ DES is similar to that of [Ch][Cl]. Therefore, the overall H-bonding ability of [Ch][Cl]-U should be lower than [Ch][Cl]. The crosslinks that endured by [Ch][Cl]-U should be less or weaker than [Ch][Cl]. In addition, if two urea molecules were inserted onto the anion, the H-bond donor and H-bond acceptor center will mainly be located on the complex anion. The existence of steric hindrance inhibited the formation of crosslink with collagen fibers. But all these theoretical analyses were different from that observed experimentally. Thereby, this theory may not properly explain the experimental phenomenon in this work.

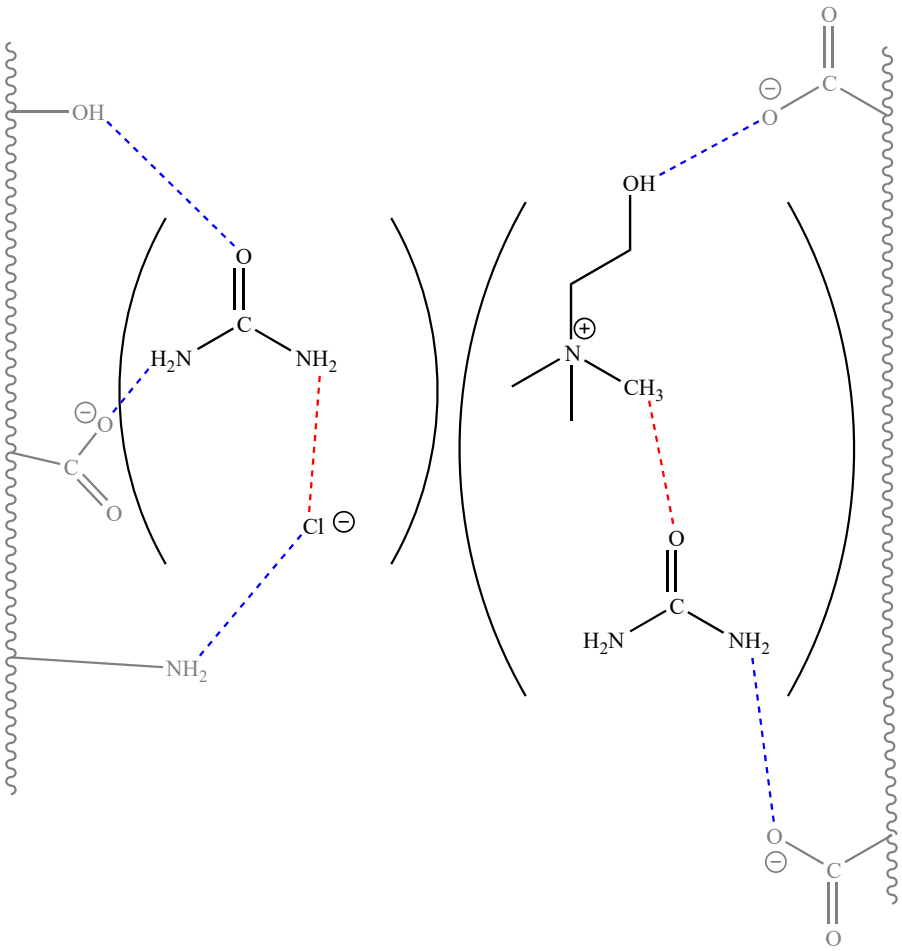

Fig. 4. Schematic diagram of interactions between ChCl-2urea DES and leather fibers. Note: grey curve, collagen fibers; red dash, intramolecular H-bonds; blue dash, intermolecular H-bonds.

The $[Ch(Urea)]^+$ $[Cl(Urea)]^-$ type structure[15] proposed by Ashworth provided an alternative approach, in which urea interacted with choline cation through carbonyl group. The complex cation formed were still able to provide strong H-bond donor ability. Whereas, after complexed with a urea molecule, the chloride still provided strong H-bond accepting ability and H-bond donating ability at the same time. Fig. 4 shown the schematic diagram of the DES-fiber interactions basing on Ashworth's theory. The complex cation and anion of DES was formed by chloride anion forms H-bond with urea molecule through amino group, and choline cation H-bonded with urea through its alkyl hydrogen. The grey chain on both sides represented the collagen fibers, which contained virous functional groups. The H-bond donor groups such as amino group and hydroxide group could interact with the complex anion. While, carboxyl groups on the fibers could interact with complex cation. The complex cation and anion paired through coulombic interaction. Therefore, multiple H-bond sites and various interactions formed between DES and collagen fibers could contribute to the formation of crosslinks. The formation of effective crosslinks improved the thermal stability and mechanism strength of leather. Therefore, this approach can be further investigated over the applications on collagen fibers.

4 Conclusions

In this work, [Ch][Cl]-U, [Ch][Cl] and U was applied for the treatment of leather. TG, DSC, burst intensity and extended height was applied for analyzing the thermal stability and mechanism strength of leather. Due to the ionic charges and H-bond effect of the treatment chemicals. Free water in treated samples could be removed at lower temperature, whereas, the removal of the boned water requires more energy. It was found that [Ch][Cl] and U filled in the gaps of fibers, without forming efficient crosslinks. Therefore, it presented minor effect in thermal stability improvement and reduced the mechanism strength. In comparison, [Ch][Cl]-U improved the thermal stability and mechanism strength at the same time. Through the mechanism analysis, it was found that [Ch][Cl]-2Urea DES system interacted with collagen fiber through [Ch(Urea)]+ [Cl(Urea)]- type structure. The DES improved crosslink with collagen fiber through amino and carboxyl groups, and therefore enhanced the thermal stability and physical strength of leather.

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