

Study on thermal degradation of cattlehide collagen fibers by simultaneous TG–MS–FTIR

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Received: 17 March 2016 / Accepted: 3 September 2016 / Published online: 13 September 2016
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Abstract Leather was useful materials since dawn of human history for excellent properties, but thermal degradation mechanism was not very clear yet. In this paper, much progress has been made in elucidating the thermal stability and thermal degradation mechanism by thermo-analytical study in argon. Thermogravimetric analysis simultaneously coupled with mass spectrometry and Fourier transform infrared spectrometry was employed to study the thermal degradation of cattlehide collagen fibers through in-depth analysis of the evolved gas. Thermogravimetry analyses carried out on sample, deprived from any residual catalyst and highlighted a two-step thermal degradation. New evidence demonstrates that the process during temperature range from 373 to 513 K was phase transformation. Photographs of polarizing microscope confirmed the conclusion. The decomposition of cattlehide collagen fibers starts at about 523 K. The cattlehide collagen fibers may undergo the process of melting, oxidation and decomposition. In decomposition, more than three steps take place. The mass spectra and Fourier transform infrared spectrometry stated clearly that double bond of carbon to oxygen, carbon to sulfur and carbon to nitrogen were destroyed firstly because the carbon dioxide, carbon monoxide and ammonia evolved simultaneously. The second peak of carbon monoxide in mass spectra indicated

that some organic fragments were decomposed above 1073 K which confirmed that thermal degradation of leather is more than three steps.

Keywords Thermal analysis · Degradation · Mechanism · Cattlehide collagen fibers

Abbreviations

TG	Thermogravimetric analyzer
MS	Mass spectrometer
FTIR	Fourier transform infrared
DSC	Differential scanning calorimetry
NCCF	Native cattle skin collagen fibers
EGA	Evolved gas analysis
DTG	Differential thermogravimetric

Introduction

Leather is an excellent material used in a variety of applications due to its durable and flexible properties [1]. The leather products (heavy leather: for soles and belts; collagen, parchments and clay light leather: tanned skin of footwear, garments and book-binding leathers) have been useful materials since the dawn of human history [2, 3]. Most of the antiques in museums are produced by leather [4]. They are valuable treasures due to the history they represent, and their preservation challenges museum custodians and private collectors alike [2, 5, 6]. Collagen is the main component of leather, and it is responsible for its thermal stability, viscoelastic properties and mechanical strength. Collagen has always been considered to be a crystalline material with defined sequences of amino acid residues, but sometimes it was regarded as semicrystalline material due to the presence of disordered regions, revealed by X-ray diffraction. Leather

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may show thermal properties associated with both crystalline and amorphous materials [7].

There are reviews focusing on the chemical deterioration of leather, according to which the degradation of leather consists in two main processes: moisture loss and decomposition [8, 9]. In general denaturation, it is generally believed that heat induced kinetic energy disrupts the secondary interactions between macromolecules, which in turn denatures the secondary and tertiary structures [10], but there is no direct identification on this phenomenon. Up to now, some works have been done on the thermal denaturation of leather [11], while less is known about the degradation mechanism of leathers [2, 12–15]. The present paper is focused on the evolved gaseous products to explore the leather thermal degradation mechanism. The combination of TG with a mass spectrometer (MS) or a Fourier transform infrared spectrometer (FTIR) allows the nature of the gaseous reaction products formed in the TG to be investigated online. The MS or FTIR can track their evolution profiles when compounds are evolved. We can know the thermal degradation mechanism of leathers by characterizing the substance or substance class through spectral interpretation and comparison with database reference spectra. Decomposition pathways can thereby be elucidated.

Experimental

The native cattlehide collagen fibers (NCCFs) provided by Sichuan University, China were subjected to thermal analysis as received. Open platinum crucible, a heating rate of 10 K min^{-1} , sample size of 10–20 mg, and flowing argon atmosphere (20 mL min^{-1}) were used for purging the thermoanalytical furnaces during the evolved gas analysis measurements.

The changes in structure of the cattlehide collagen fibers were monitored using an Olympus BX-51 polarizing microscope. Samples were placed between two thin glass slides and heated on a programmable hot stage at a heating rate of 5 K min^{-1} to 513 K. Subsequently, the samples were kept at temperature 303, 373, 423, 473, 488, 493, 503 and 513 K for about 5 min to eliminate heat history and observe the structure modification.

The TG–EGA–MS–FTIR apparatus consists of a SETSYS Evolution 16/18 Thermogravimetric Analyzer (SETRAM Instrumentation Inc.), OmniStar (Pfeiffer) and a Tenso27 (Bruker) FTIR spectrophotometer equipped with a TG/IR Accessory gas cell. The furnace and the gas cell were coupled through a heated ($T = 553 \text{ K}$) 0.8-m stainless steel tube with diameter of 3 mm. The OPUSTM software accumulated 40 interferograms in every second, and they were transformed to one IR-spectrum

($600\text{--}4000 \text{ cm}^{-1}$). Temperature calibration was carried out with indium. Baseline curves were measured under the same experimental conditions. The FTIR spectrometer obtained spectra every 7 s to determine the evolution rate and composition of several compounds quantitatively. Some experiments were repeated three times to determine their reproducibility, which was found to be good. Species identification and analysis were discussed in some detail below. The components of released gaseous mixtures had been monitored and identified mostly on the basis of their FTIR and MS reference gas spectrum available on NIST mass spectrometry library and EPA.

Results and discussion

Simultaneous TG/DTG curves of NCCF measured in argon

The simultaneously recorded TG and DTG curves are shown in Fig. 1a indicating two significant mass loss steps during decomposition in argon. Typical mass loss data for the thermal decomposition of leather in inert argon atmosphere are shown in Fig. 1b. The first stage occurred between ambient temperature and 393 K, indicating about 4.8 % loss in mass, denoted by step I. The mass loss in this stage is because of the loss of moisture. The second step appeared to be more complex with a major peak observed at 503 K. The mass loss between 493 and 923 K was 61.79 % of the original mass. This step was denoted by II. The maximum mass loss is because of the thermal decomposition of hide powder that happen within temperature ranging from 593 to 823 K. This decomposition curve is formation and evaporation of some volatile compounds from the hide powder.

Figure 1a, b shows cattlehide collagen fibers heated in argon atmosphere. Figure 1c shows the TG–DSC curves of cattlehide collagen fibers obtained by analysis in N_2 . The samples exhibited three endothermic peaks and two exothermic peaks. The peak at 481 K corresponds to the crystallinity of the sample, which could be explained by the biphasic amorphous–crystalline structure of leather, according to which the crystalline triple helix is embedded into an amorphous matrix [12, 16]. The peak at 573 K corresponds to the decomposition of hide powder. The decomposition does not occur at a uniform rate, and thus some leathers are degraded during early decomposition, while others are degraded later. The mass loss of this process was up to 61.79 %. The peak at 710 K, suggesting a highly destabilized structure with a large distribution of components, corresponds to the decomposition of some organic fragment. A further support for this explanation is the mass spectrometric evidence of the $m/z = 28, 30 \text{ amu}$

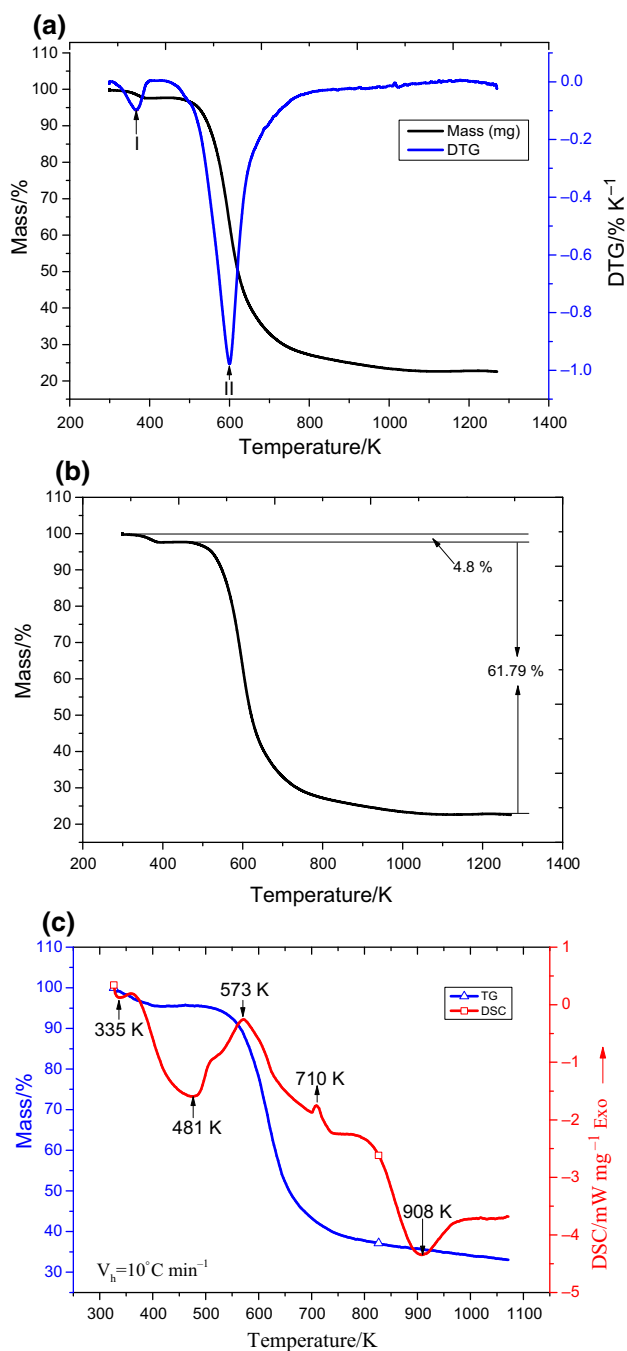


Fig. 1 a TG and DTG curves of cattlehide collagen fibers, b Mass loss for the decomposition of cattlehide collagen fibers and c TG-DSC curves of cattlehide collagen fibers

peak appeared at 743 K, as shown in Fig. 3. The peak at 908 K corresponds to the carbonization of tar. According to our previous results obtained by TG analysis of hide powder, no mass loss occurred above 908 K [17].

The photographs in Fig. 2 showed that there is no obvious change below 473 K. The bright area is ordered structure of leather, and dark one is amorphous structure.

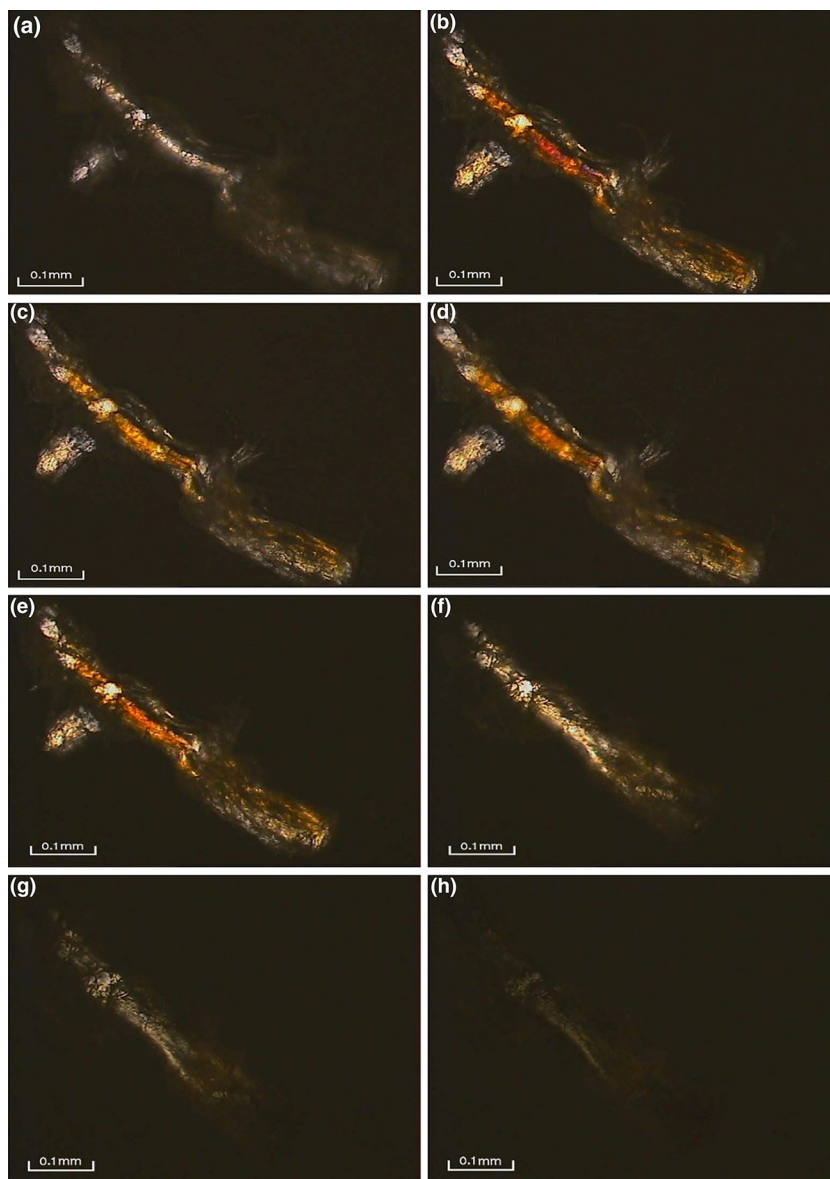
The photographs confirmed that there are two phases in leather. Nearly all the bright area disappeared when the temperature rose up to 513 K. The endothermic peak in Fig. 1c at 481 K demonstrates that the process is melting. The 61.79 % mass loss in TG curve started at about 523 K. In conclusion, the above results confirmed that the structure of leather was transformed from crystalline or semicrystalline to amorphous. It is obviously that only phase transformation happened when the temperature ranges from 373 to 513 K. So the decomposition of leather was happened above 513 K, we can infer from Fig. 1 that the decomposition of leather started at about 523 K.

Evolved gas analysis of NCCF by online coupled TG-EGA-MS-FTIR

A limited number of mass units ($m/z < 100$) were selected to analyze in this paper. The selected mass spectrometric evolved gas has helped us to observe evolution of leather decomposition. Beyond the known H₂O and CO₂, there are some new gaseous species represented by $m/z = 30$, assigned to NO, CH₂O, C₂H₆ and 67 to C₄H₅N, respectively [18].

The first mass loss (step I) in the decomposition curves of cattlehide collagen fibers in inert atmosphere occurred around 373 K, and 18 amu peak assigned to the loss of water, notably molecular adsorbed water. It is obviously that 18 amu peak is below 373 K and, therefore, at slightly higher temperature than the step I of DTG peak. There may be a delay in transfer from the capillary to the MS. These new species evolved at step II, and a number of m/z peaks were chosen as representative of the decomposition products observed in this step. Peaks chosen for analysis were at 28, 30, 32, 44, 54, 64, 67, 70, 72, 78, 81 and 91 amu. Further heating results in the thermal decomposition of the leather in step II were observed in the DTG as a peak at 573 K. The most of decomposition products were evolved at stage II. The 28 amu fragment has two peaks in the curve. First one appeared simultaneously with 32 amu and 44 amu, and the second one come into sight above 1000 K. The 32 amu fragment was assigned to oxygen, which decreased from step II, because oxygen might react with nitrogen or carbon monoxide. The 44 amu curve decreased sharply at around 553K, there are some carbon dioxide in the beginning, and part or most of carbon monoxide in the early stage was oxidized to carbon dioxide, while oxygen was used up in the later. At step II, the peak in the 44 amu curve was observed to begin at around 593 K. There are two peaks in 18 amu curve. The first one is water desorption, and the second peak may be oxidation product. The 44 amu curve was assigned to predominantly carbon dioxide, and the 30 amu curve assigned to nitric oxide. The 64 amu curve was associated with a series of organic

Fig. 2 POM photographs of cattlehide collagen fibers at different temperature: **a** 303 K, **b** 373 K, **c** 423 K, **d** 473 K, **e** 488 K, **f** 493 K, **g** 503 K and **h** 513 K



products. Possible molecular identities and assignments of these evolved species were based on the molecular mass, and the peaks were reported in the literature for the pyrolysis of a variety of organic matters and are listed in Table 1.

The 12, 16 and 18 amu fragments were evolved below 573 K. Above 593 K, the rest of the selected fragments appeared, which shows that the small molecules evolved at first, and the decomposition happens higher than 573 K. The 28 amu fragment (Fig. 3a) was assigned to CO and N₂, respectively, which evolved continuously and had two peaks at 593 and 1173 K. The mass peak coanalyzed with FTIR spectroscopy of the evolved product at 1173 K was N₂ the

most possible. As the N₂ was not absorbed by FTIR, and there is no peak in the FTIR curve at 1173 K. Among the organic fragment curves, the 70, 72 and 78 amu curves (assigned to benzene) show a distinct broad peak in this region.

Although the data in Fig. 3 were recorded in an inert atmosphere, the purge gas still contains a small amount of oxygen (<10 ppm). That small contamination in the purge gas can be used to aid the identification of the origin of CO₂ evolution in step II due to the decomposition of the organic pyrolysis products. The peaks in the 44 amu curve should be CO₂. Peaks are observed in the 32 amu curve, corresponding to oxygen, suggesting that a significant portion of mass loss in step II associated with the removal

Table 1 Evolved gas analysis

Fragment/amu	Molecular formula	Molecule	References
16	CH ₄	Methane	[19]
18	H ₂ O	Water	[19]
28	N ₂ , CO	Nitrogen, carbon oxide	[20]
30	CH ₂ O, C ₂ H ₆	Formaldehyde, ethane	[20]
32	O ₂	Oxygen	
44	CO ₂	Carbon dioxide	
54	C ₄ H ₆ , HCCCHO	Butadiene, cyclobutene, butyne Propynal	[21]
	C ₃ H ₅ N	Propane nitrile	
64	SO ₂	Sulfur dioxide	
67	C ₆ H ₁₀	Crotonitrile, allyl cyanide, methacrylonitrile	[21]
70	C ₅ H ₁₀ , C ₄ H ₆ O	Pentene, cyclopentane	
72	C ₅ H ₁₂ , C ₃ H ₄ O,	Pentane, acrylic acid	
78	C ₆ H ₆	Benzene	
81	C ₅ H ₇ N, C ₇ H ₁₂	Methyl pyrrole, methyl cyclohexane	
91	C ₂ H ₅ NO ₃ ,	2-nitroethanol, ethyl nitrate	
	C ₆ H ₅ CH ₃ ,	Toluene	
	C ₆ H ₄ (CH ₃) ₂ ,	1,4-, 1,3- and 1,2-dimethyl benzene	
	C ₆ H ₅ -C ₂ H ₆	ethylbenzene	

of the organic phases. Carbon monoxide loss was observed at a high temperature, probably attributed the decomposition of the organic phase.

Figure 4a shows that there are two major peaks in 28 amu fragment curve. The first peak started at about 513 K, decreased about half at 658 K and decreased totally at 713 K. The second peak started at 1033 K and end at 1373 K. The result demonstrated that carbon monoxide evolved continuously and was the major pyrolysis product. Figure 4b shows the mass spectroscopy of 30 amu fragment. The 30 amu curve has been tentatively assigned to both the production of nitric oxide (NO) and formaldehyde. Both are possible products of the pyrolysis of proteins and amides. Ethylene with the *m/z* of 30 amu and could, therefore, also contribute to this evolution. The 30 amu has a number of peaks at around 598, 748 K with a series of shoulders associated with each peak.

It is also interesting to note the continuous evolution of 30 amu. That may due to the occurrence of gas phase reactions, although it is notable that the DTG curve in this region does not return to 0 % min⁻¹, a significant and finite minimum indicates that material is continually lost throughout this region. Without further analysis, however, identification of the species responsible for this peak cannot be made with certainty. Identity and evolution dynamics of the evolved gaseous species have also been

described by means of online coupled FTIR gas cell and spectrometer.

TG–FTIR and TG–MS extend the thermal analysis by additional monitoring and identification of the pyrolysis gases, comparing TG illustrates the thermal decomposition in terms of the mass loss. It is obvious that such a characterization of the decomposition profits greatly with this additional information and delivers a detailed insight into the decomposition processes. However, the interpretation of the FTIR is often difficult since a superposition of the various signals from the different gases can lead to complex spectra. In the case of TG–MS, the ionization of the decomposition fragments can result in ambiguous mass signals. By using both methods, unambiguous interpretations of the data were obtained without using further assumptions on the material or the active decomposition pathway. Figure 5a is a three-dimensional plot of the FTIR spectrometry response during such a heating experiment to 1473 K at 10 K min⁻¹. A characteristic spectrum obtained at 673 K is shown in Fig. 5b. The decomposition processes of leather have occurred in our simultaneous and online measurements resulting in two mass loss stages at 363 and 593 K, respectively, producing in both cases H₂O, NO, CH₂O, C₄H₅N and C₂H₆. The first stage corresponding to moisture (series of narrow bands at 4000–3500 and 2000–1300 cm⁻¹) is evident. On subsequent heating, a

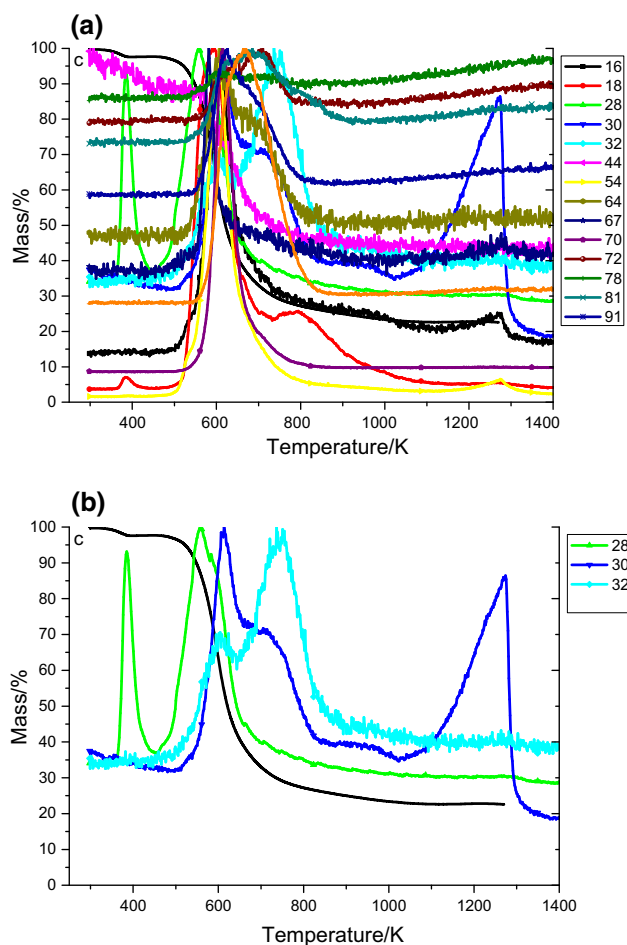


Fig. 3 Ion current, as a function of the m/z ratio in amu from 2 to 100 amu over the full temperature range (room temperature to 1373 K). **a** Only m/z ratios up to 100 are shown as no observable ion current was measured above this value. **b** Mass spectroscopy of $m/z = 28, 30$ and 32 amu fragment and DTG curve of sample

further and more intense evolution of H_2O is observed, reaching a maximum at 556 K, due to condensation reactions. Ammonia, with a characteristic bands at 964, 930 (main bands), 1626 and 3335 cm^{-1} starts to evolve above 523 K. Between 523 and 503 K, its bands are the most intense, suggesting that deamination might be the dominant decomposition process in this temperature region. Ammonia originates from deamination reactions of collagen involving free $-\text{NH}_2$ groups from arginine and lysine and peptide $-\text{NH}-$ groups. After reaching a maximum release at 513 K, the intensity of NH_3 bands diminishes and then slightly decreases at high temperatures. It is noteworthy to mention that nitrogen can also be released from leather as N_2 which is not detectable by FTIR. The most intense band in 3D FTIR plots is that of CO ($2150\text{--}2300\text{ cm}^{-1}$) which becomes visible at around 523 K and sharply increases up to 613 K. After falling to a broad

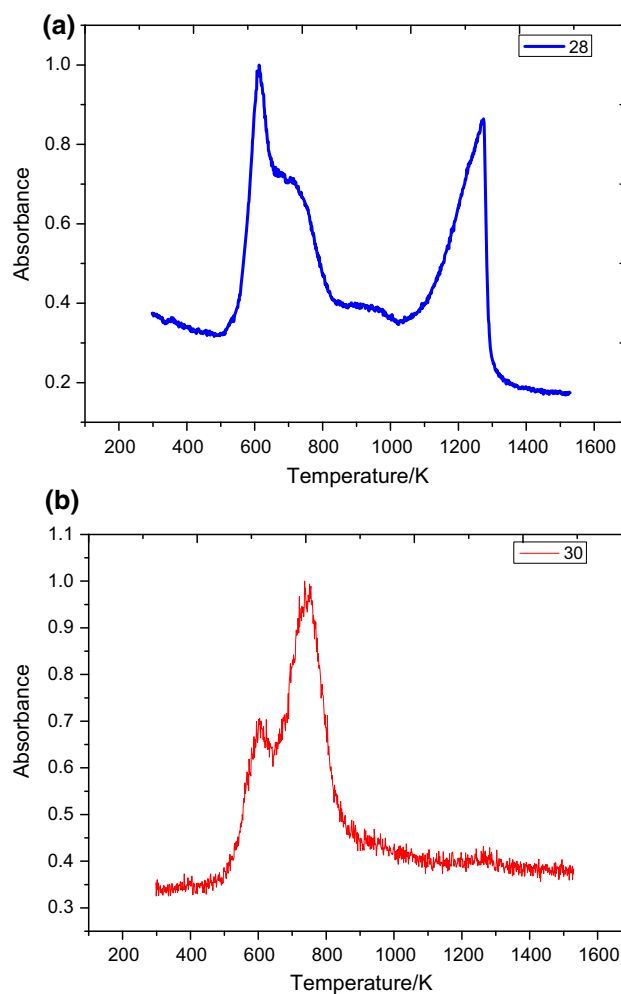


Fig. 4 Mass spectroscopy of 28 amu fragment (**a**) and 30 amu fragment (**b**)

minimum at 823 K, a slight increase is observed at 1273 K. Carbon monoxide can originate from direct decarboxylation of free $-\text{COOH}$ groups from glutamic and aspartic acids. We believe that this reaction is responsible for the incipient release of CO. Afterward, CO may be produced by decomposition reactions involving peptide $-\text{CO}-$ groups. The final slight increase in CO evolution must be due exclusively to condensation reactions within the residues. The decomposition of sample at 593 K might be either a breaking up process of macromolecule following gas phase oxidation or bulk catalyzed dissociation. The catalyst itself is probably an in situ formed solid decomposition intermediate of leather.

A typical spectral output from the TG-FTIR is shown in Fig. 5a, which was known as a stack plot, providing information both as a function of wavenumber and temperature. Above 573 K, the evolution of HNCN (2250 cm^{-1}) can be detected (maximum at 613 K).

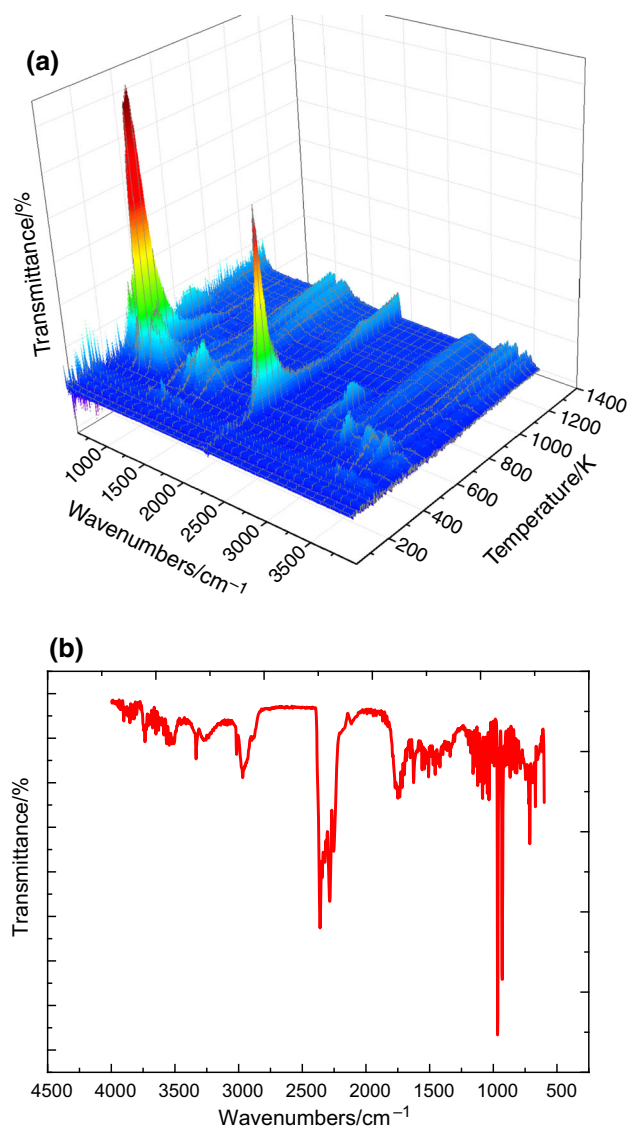


Fig. 5 **a** FTIR spectra collected during the online analysis of the volatiles evolved in the decomposition of the hide powder, **(b)** FTIR spectrum of evolved gases from leather, decomposed in argon, measured at 773 K by online coupled TG–EGA–FTIR system (initial mass 12.96 mg, 20 mL min⁻¹ argon flow, 10 K min⁻¹ heating rate, open Pt crucible)

However, the corresponding band is partially superimposed on CO₂ band, resulting in an augmented intensity. Pyrrole (C₄H₅N) was detected to evolved above 523 K, with a peak at 613 K, but its band (720 cm⁻¹) partially overlaps with a minor band of CO. Pyrrole was previously detected by Py-GC/MS as a major compound from pyrolysis of pig-skin collagen, leathers and bones [22]. Pyrrole originates from proline, which is the second most abundant amino acid in collagen. At above 643 K, a band corresponding to HCN (714 cm⁻¹) appears, reaching a very broad maximum between 573 and 773 K. At higher temperatures, a broad

band at 2850–3000 cm⁻¹, with a highest peak at 2970 cm⁻¹ reaching a maximum release at around 773 K, was attributed to hydrocarbons, mainly ethane. The FTIR results at 673 K in argon conditions, shown in Fig. 5b, confirmed the presence of a second degradation step, during which the characteristic narrow peaks of CH₄ (1304 cm⁻¹) can be easily observed, which have a maximum intensity at around 493 K. Methane may form by condensation reaction involving –CH₃ and –CH₂– groups. It is interesting to note that the maximum CH₄ release coincides with a slight minimum in CO evolution. The above-mentioned compounds (except pyrrole) were also detected on thermal decomposition of another protein, casein. Other compounds which were observed on thermal decomposition of bone collagen or biocollagenic wastes by MS [15, 23–26] could not be clearly distinguished in our FTIR study due to the fact that their absorption bands are overlapped on the infrared bands of the above-mentioned gases. As a matter of fact, a black solid residue was yielded during the pyrolytic degradation of the leather. Detailed data about decomposition temperatures and volatile loss could be obtained from the analysis of the experimental runs performed. These uncertainties have been resolved by FTIR spectroscopic gas cell (TG–FTIR), showing only evolution of NO₂ with two absorption bands positioned at 1616 and 2911 cm⁻¹, and no bands of NO or N₂O could be detected, considering the expected nitrogen oxides.

Conclusions

In this preliminary study, TG–MS–FTIR was applied to the characterization of leather fragments. The aim of this initial study was to characterize the decomposition evolved products of the leather fragments and interpret the TG–MS–FTIR data. TG–MS–FTIR curves were collected by heating leather samples to 1273 K in an argon atmosphere. Under these conditions, both the organic and inorganic phases decomposed and produced a variety of organic fragments and carbon monoxide. At first, water was lost at about 373 K, and meanwhile, triple helix was destroyed. Second, long chains were fracture. Long chains were decomposed to inorganic fragments and organic fragments, while some ring compounds were not decomposed at about 593 K, because some fragment as pentene and cyclopentane were evolved in the later. It demonstrated that leather was decomposed three or more steps. Pyrolysis of the organic phase, which is composed predominantly of collagen, resulted in the observation of ion fragments up to 100 amu. Selected fragments were monitored and could be associated with the decomposition of the collagen phase. By targeting changes in particular decomposition fragments, it may be possible to determine thermal degradation

mechanism of leather. The method shows TG–MS–FTIR as an approach to the study of leather degradation in a forensic context. Further TG–MS–FTIR studies on different tanned and artificial ageing leather are being undertaken. The leather samples will also be studied in different atmospheres in order to gain a more detailed understanding of the decomposition processes of forensic leathers. The TG–FTIR technique proved to be a straightforward experimental methodology to achieve efficient data on the nature of the evolved gas products generated in specific pyrolytic conditions.

Acknowledgements This research was financially supported by the National Natural Science Foundation of China (No. 51373158) and K. C. Wong Education Foundation, Hong Kong. Beifang University of Nationalities, China (No. 2014XBZ12).

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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