

Synergistic interactions in the thermal decomposition of leather and PVC mixtures

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ABSTRACT

The problem of mixed leather waste (natural and artificial) is recognized as a significant issue in industrial recycling, since the separation of these materials is challenging. However, thermochemical conversion is widely researched as a feasible method for dealing with such a complex waste stream. Deeper understanding of the interactions between the components during thermal decomposition and the effect of the reactive hydrogen chloride evolving from PVC (a usual component of artificial leather) should be considered in the planning of thermal recycling processes, and therefore, these findings can be of interest to users and manufacturers. In this paper, co-pyrolysis of PVC and natural leather was investigated by thermogravimetry/mass spectrometry (TG/MS) and pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) methods. The study revealed the mutual influence of PVC and proteinaceous materials, such as leather, during thermal decomposition. The thermal stability of PVC decreased in the presence of leather, as the dehydrochlorination step shifted to lower temperatures by 20–30 °C, regardless of the tanning type of leather. Conversely, the thermal decomposition of leather was altered by the presence of PVC, favoring fragmentation reactions over depolymerization, which resulted in the formation of more hydrogen cyanide and acetonitrile but less diketopiperazines (DKPs). The effect of hydrogen chloride released by PVC in these processes was further studied by the pyrolysis of a model sample, which confirmed the primary role of hydrogen chloride in the increased hydrogen cyanide and acetonitrile evolution. The formation of mono- and polyaromatic compounds was increased slightly during pyrolysis of leather–PVC mixtures, which could contribute to the decreased char yields of the mixtures measured by TGA.

1. Introduction

Leather and polyvinyl chloride (PVC) are among the most prominent materials widely used in automotive, furniture and fashion industries. Natural leather offers durability, breathability, and a premium appearance; however, its high cost and limited availability constrain its widespread application. PVC leather provides water resistance, easy cleaning, and visual similarity to natural leather at a significantly lower price. The global production of natural leather exceeds 2 billion m² per year [1], while PVC leather production exceeds 1 billion m² annually and continues to increase. Co-usage of PVC leather and natural leather is common in automotive, furniture and fashion industries, e.g. car seats or sofas often use natural leather on contact surfaces and PVC leather on

less visible areas such as sides and backs. Similarly, bags and footwear often combine natural and PVC leather panels. This approach reduces overall manufacturing costs while maintaining the premium appearance. Besides simple combination of natural and PVC leather, the use of both natural and artificial leather containing composite materials, like laminated leather or hybrid leather [2,3] is also expanding [4], and further complicating end-of life management. Consequently, industrial and consumer waste streams increasingly contain inseparable mixtures of natural leather and polyvinyl chloride (PVC), posing pressing scientific and technical challenges for end-of-life management. As environmental concerns rise, managing waste from leather and polyvinyl chloride (PVC) becomes increasingly critical.

Leather, made from animal hide, undergoes tanning to enhance its

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durability, and resistance to decomposition and microorganisms. Two primary tanning methods are used: chromium tanning [5,6] and vegetable tanning [7,8]. Chromium-tanned leather is valued for its superior suppleness, thermal stability, and resistance to wear and environmental factors [9,10]. It is produced with chromium salts, especially chromium (III) sulfate, which cross-link collagen fibers to create a stable and resilient material. Vegetable tanning uses natural tannins from plant sources such as tree bark and leaves [11,12]. This method gives leather a firmer texture and is favored for its eco-friendliness and traditional craftsmanship, but it is expensive. As chromium tanning faces stricter regulations and environmental scrutiny due to hazardous waste and possible formation of carcinogenic chromium(VI), vegetable and aluminum mixed tanning is gaining attention for reducing environmental hazards, supporting circular economy goals, and meeting growing consumer demand for sustainable products.

As an alternative to natural leather, artificial leather is made of synthetic polymers, especially PVC, valued for its versatility, durability, and cost-effectiveness. These properties make it a common choice in manufacturing, construction, consumer goods, and artificial leather. The chlorine content in PVC contributes to its chemical resistance and flame retardancy, while its semi-crystalline nature enhances its mechanical strength and toughness [13]. This plastic is widely used for its chemical resistance and mechanical properties, while is often applied with other natural [14–16] and artificial materials [17–19]. PVC is a well-characterized polymer, but recycling and waste management are challenging, especially in mixtures [20–23].

Natural and artificial leathers are often used together in various applications. Some industrial processes produce waste as mixtures of both types, making separation challenging. Thermochemical conversion offers a solution for utilizing such waste mixtures without separating the components. Thermoanalytical techniques provide effective methods for analyzing the thermal decomposition of mixed samples [24–26].

The thermal decomposition of the main collagen-based materials, i. e., leather and parchment has been extensively studied. The main decomposition products of the fast pyrolysis of these materials are 2,5-diketopiperazines (DKPs), which are cyclic dimers of amino acids deriving from protein chains [27,28]. Smaller nitrogen-containing molecules also evolve by fragmentation (e.g., ammonia, hydrogen cyanide, acetonitrile, and pyrrole). According to our latest study [29], the yield of hydrogen cyanide and acetonitrile increased in the presence of chromium, while the evolution of ammonia was hindered.

Few papers discuss the co-pyrolysis of leather with various materials. Liu et al. [30] pyrolyzed chrome-tanned leather with lignocellulosic wheat straw. They found that adding wheat straw reduced the average activation energy required for leather pyrolysis; but increased the yield of solid residue.

The thermal decomposition of PVC presents significant challenges, especially regarding environmental impact and safety concerns. The dehydrochlorination of PVC occurs at around 300 °C forming hydrogen chloride, aromatic hydrocarbons (mainly benzene) and remaining polyene chains [31–33]. At higher temperatures, cracking and cross-linking of the polyenes produce substituted mono- and poly-aromatic hydrocarbons, and a solid carbonaceous residue [17,34]. Co-pyrolysis of PVC mixed with other materials is an extensively studied research field [35–38]. The thermal decomposition of PVC mixed with wood, a lignocellulosic biomass, was studied under slow and fast heating [14]. In the presence of PVC, the cellulose content of wood decomposed at lower temperatures. Significant amounts of chloromethane also evolved from the PVC–wood mixtures during pyrolysis, while hydrogen chloride formation was significantly reduced.

While the thermal decomposition of these materials has been individually explored, their mutual interactions during co-pyrolysis, and the resulting shifts in product spectrum, remain poorly understood. Only a few papers deal with the co-utilization of PVC and leather. Madera-Santana et al. [39] extruded PVC with leather and performed the mechanical characterization of the composite. The moisture absorption and

tensile properties of the composites were found to be suitable for industrial use such as shoe manufacturing. Tang et al. [40] investigated the co-combustion of PVC, rubber and leather mixtures under different oxidative atmospheres. They established that the interaction between PVC and leather hindered the burnout of the blends. However, to the best of our knowledge, the pyrolysis of PVC-leather mixtures has not been investigated yet.

Thermochemical conversion offers a promising route for valorizing mixed waste without separation. In industries like automotive and fashion, these materials often result in inseparable waste due to diverse manufacturing processes generating mixed material scraps. Analytical pyrolysis offers resolutions for tracing volatile decomposition products and elucidating underlying decomposition pathways. This paper focuses on the thermal behavior of PVC–leather mixtures to understand the primary decomposition routes and interactions between the components.

This study aims to fill the knowledge gap by systematically examining the co-pyrolysis of PVC and differently tanned leathers. By investigating thermal behavior, component interactions, and product distribution, we seek to provide information critical for designing safer, more efficient valorization and recycling routes for mixed biopolymer–plastic waste. As research progresses, these insights could lead to innovative approaches in large-scale industrial applications, promoting a future where sustainable waste management becomes the industry standard.

2. Materials and methods

2.1. Materials

The leather samples were prepared in the Leather and Footwear Research Institute (ICPI) of the National Research and Development Institute for Textile and Leather (INCOTEX) in Bucharest, Romania. The list of leather samples used, along with their designation, is shown in Table 1. The proximate analysis data and the nitrogen content of the leather samples are summarized in Table S1 of the Supplementary material. More detailed analysis of the composition of pure leather samples can be found in our earlier work [29]. As a model material for artificial leather, coarse powder of plasticizer-free PVC (Vinoflex S5715, BASF) was used.

The leather samples were cut into pieces of nearly 4 × 4 mm squares. All the leather samples and PVC were frozen in liquid nitrogen and then cryo-milled in a Retsch MM301 ball mill (Germany) to fine powder. After that the ground leather and PVC samples were mixed in a ratio of 1:1 and 3:1 by mass. Though the leather–PVC ratio varies widely in industrial applications, the ratios applied in this study were chosen to assure the possibility of apparent interactions and to represent potential waste streams, where leather and PVC may coexist. Sample designations indicate the composition and ratio: e.g., LMM–PVC,3:1 refers to a mixture of mimosa-tanned bovine leather (LMM) and PVC in a ratio of 3:1. The ratio 1:0 is used for samples containing only leather with no PVC added. For the preparation of the model mixture of LMM with hydrochloric acid, labelled as LMM+HCl, concentrated hydrochloric acid (37 %, reagent grade, Scharlau) and deionized water were used.

Table 1
Designation of the feedstock samples.

Material	Abbreviation
Chrome-tanned bovine leather	LCR
Aluminum- and myrobalan-tanned bovine leather	LAY
Mimosa-tanned bovine leather	LMM
Polyvinyl chloride	PVC

2.2. Methods

2.2.1. Inorganic content analysis

Approximately 0.5 g of the leather sample was weighed into glass beakers. For digestion, 10 mL nitric acid (67 % *m/m*, AR grade) was added to the samples and covered with watch glass plates. The sample was boiled for 4 h using a hot plate to ensure complete digestion. Thereafter, the solution was cooled and filled up with ultrapure water (ELGA, 18.2 MΩ cm) to a volume of 25 mL. The content analysis of the solutions was performed using inductively coupled plasma–optical emission spectroscopy (ICP-OES) with a Spectro Genesis ICP-OES simultaneous spectrometer featuring axial plasma observation (Germany). A multi-element standard solution (33 elements, M8A96.K1.5N. L5, CPAchem Ltd.) was applied for calibration. At least three parallel measurements were performed.

2.2.2. Thermogravimetry/mass spectrometry (TG/MS)

Thermogravimetry/mass spectrometry experiments were conducted with a Perkin-Elmer TGS-2 thermobalance (USA). The device featured a modified furnace and a temperature controller (Eurotherm, UK). It was coupled to a HiQuad quadrupole mass spectrometer (Pfeiffer Vacuum, Germany). About 1.5 mg sample was placed in a platinum sample pan. The heating rate was 20 °C min^{−1} from room temperature to 950 °C under helium atmosphere at a flow rate of 140 min^{−1}. A portion of the evolved gases and vapors were introduced into the MS through a glass-lined metal capillary transfer line heated at 300 °C. The MS ion source was operated at an electron energy of 70 eV. The mass range of 14–150 Da was scanned for 25 s in each cycle. The signal of *m/z* 17 was corrected by subtracting the calculated contributions from water fragments from each measured value. Thus, the presented *m/z* 17 ion curves illustrate exclusively ammonia formation in the TG/MS plots. Ion intensities from TG/MS measurements were normalized by sample mass. This normalization ensures comparability, and corrects sample variability, thereby enhancing the accuracy of the analysis.

2.2.3. Pyrolysis–gas chromatography/mass spectrometry (Py-GC/MS)

Pyrolysis–gas chromatography/mass spectrometry measurements used a Frontier Multi-Shot Pyrolyzer (EGA/PY-3030D, Japan) connected to an Agilent 6890A/5973 GC/MS (USA). About 0.4 mg of the sample was pyrolyzed at 500 °C (calibrated temperature) for 30 s in helium atmosphere. The furnace was flushed with a gas flow rate of 100 min^{−1}. For the LMM+HCl sample, 1 µL hydrochloric acid of 3.7 % *m/m* was added to approximately 0.2 mg ground leather weighted into a stainless-steel sample cup. The mixture was kept at 50 °C in a furnace for 30 min before the Py-GC/MS measurement. A DB-1701 capillary column (30 m length, 0.25 mm i.d. and 0.25 µm film thickness) separated the pyrolyzate components. The GC oven was set to hold at 40 °C for 4 min then the temperature was raised at 10 °C min^{−1} to 280 °C and held for 7 min. The MS ran in electron ionization mode at 70 eV, scanning *m/z* 14–500. The identification of the molecules was based on the combined Wiley Registry 9th edition/NIST 2011 mass spectral library and literature data [27,41–43]. The integral data for chloromethane, hydrogen cyanide and benzene were evaluated based on the peak integral of the single ion chromatograms of *m/z* 50, *m/z* 27, and *m/z* 78, respectively. Triplicate measurements were carried out with each sample and the integrated peak areas were normalized by the sample mass.

3. Results and discussion

3.1. Inorganic contents of the leathers

ICP-OES measurements were performed to determine the inorganic content of the leather samples. The metals used during the tanning process were also quantified and the results are presented in Table 2. Detailed ICP-OES results of the same leather samples can be found in our earlier work [29]. The high chromium content of LCR apparently derives

Table 2

Concentrations of a few significant inorganic elements present in leather samples with standard deviation (SD).

Element	Sample					
	LCR		LAY		LMM	
	Mean (mg/g)	SD (mg/g)	Mean (mg/g)	SD (mg/g)	Mean (mg/g)	SD (mg/g)
Cr	18.7	0.3	0.050	0.002	0.040	0.002
Al	0.007	0.001	9.6	0.2	0.036	0.003
Ca	0.07	0.03	0.359	0.005	1.25	0.09
K	0.018	0.006	1.90	0.03	0.045	0.003
S	9.1	0.3	3.6	0.1	2.7	0.2

from the chromium sulfate tanning agent, while the aluminum and potassium contents of LAY originate from the potassium aluminum sulfate tanning agent. The liming phase is one of the main steps in leather production to separate the hair from the hide. After liming, different amounts of calcium remained in the leather depending on the type of further tanning procedure. The vegetable tanning process does not require low pH; therefore, significant amounts of calcium remained in LMM. Aluminum and chromium tanning procedures use more acidic media which leach lime more efficiently; therefore, the calcium content of LAY and LCR is lower.

The sulfur content of leather samples originates from various sources. Sulfur-containing amino acids are present in proteins [44–46]; however, the sulfur content of proteins is very low. Higher amounts of sulfur compounds are introduced into leather during the tanning procedures. LCR sample has sulfur content derived from chromium sulfate used in the tanning process. LAY sample contains remnants of alum (potassium aluminum sulfate). LMM sample contains mainly sulfonate surfactants used in the vegetable tanning process. The residues of sulfonate and sulfate compounds release SO₂ during thermal decomposition, while the methionine residues of proteins produce mainly methanethiol [29]. As Table 2 shows, LCR sample has the highest amount of sulfate remnants followed by LAY.

These elemental distributions have practical implications; for instance, high chromium content impacts both leather durability and environmental safety, necessitating careful management. High calcium content may influence the softness and flexibility of the leather products, which could be critical depending on the leather's intended use. Elevated chromium levels may lead to toxicity for plants, microorganisms, and animals, potentially disrupting ecosystem functions and food webs. Addressing these concerns requires careful monitoring and management strategies to mitigate chromium contamination and its environmental impact.

3.2. Thermal decomposition of leather–PVC mixtures

To reveal component interactions in the leather–PVC mixtures that occur during thermal decomposition, the measured thermogravimetric (TG) curves of mixtures were compared with the calculated curves. The TG curves of a mixture can be modeled from the measured curves of the individual components assuming no interaction between components. These curves of the different mixtures were calculated as linear combinations of the TG curves of leather and PVC samples in the ratio of the components present in the mixture.

Fig. 1 shows the measured and calculated TG and DTG curves of the leather–PVC samples mixed in a ratio of 1:1 and 3:1. The comparison of the measured and calculated TG curves clearly shows that some interactions were present between the components during the thermal decomposition of the mixtures in each case. The calculated TG and DTG curves of the mixed samples were calculated according to the mixing ratio; e.g., if a sample was a mixture of one part of PVC and one part of leather (50 % and 50 %), then the measured TG and the DTG curves of the pure components were multiplied by a factor of 0.5 and 0.5,

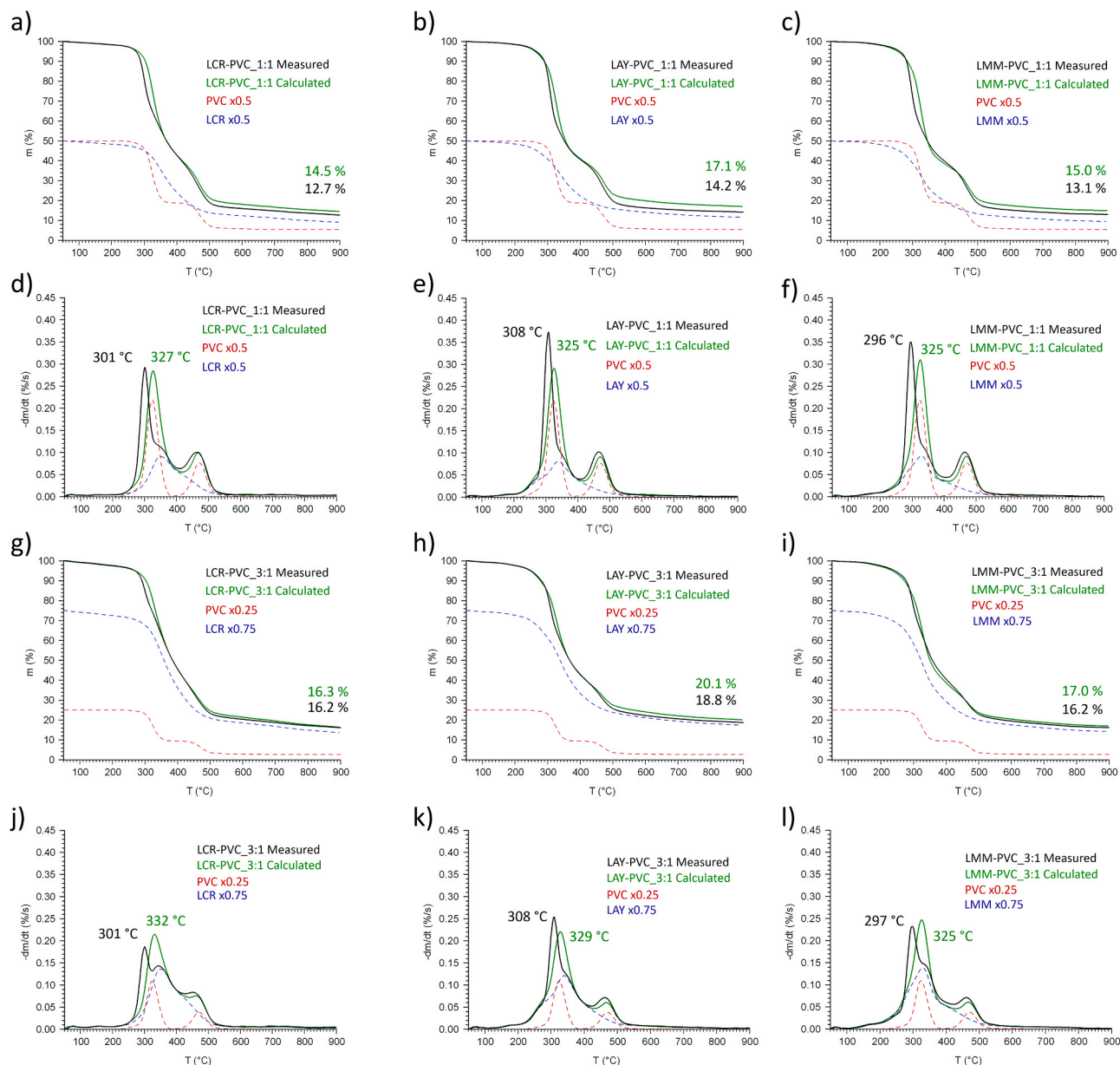


Fig. 1. Measured and calculated TG and DTG curves of the leather–PVC mixtures prepared in the ratios of 1:1 and 3:1. The dashed lines indicate the measured TG and DTG curves of the components used for the calculated mixture curves.

respectively and summed up. If a sample was a mixture of one part of PVC and three parts of leather (25 % and 75 %), then the measured TG and DTG curves of the pure components were multiplied by a factor of 0.25 and 0.75, respectively and summed up. The most remarkable difference between the measured and calculated curves is the shift of the first decomposition step to lower temperatures and the decreased amount of carbonaceous products remaining after the complete degradation of the mixtures. The amount of char was measured 2–3 % lower in the leather–PVC 1:1 mixtures than expected based on the calculated curves. This reduction could potentially lead to decreased solid waste output and enhance the environmental performance of the disposal process. In addition, a small increase in the mass loss rate was also measured, except in the case of LMM–PVC 3:1. These effects can be observed regardless of the tanning type of the leather component and the mixing ratios.

For the detailed explanation of the thermal degradation of the mixtures, the evolution of some breakdown products was monitored by the MS detector of the system. The results show that after the evaporation of

the adsorbed moisture content, the mass loss rate started increasing before the temperature reached 200 °C, indicating the devolatilization of water tightly bound to the structure of collagen [29]. The measured and calculated curves do not diverge below 250 °C, indicating no significant interaction between the components below this temperature. The thermal behavior of the mixtures measured above 250 °C, however, differed from the calculated curves. The mass loss rate of each leather–PVC mixture peaked at lower temperatures than their calculated DTG curves. The temperature of the maximal rate of decomposition shifted to 25–30 °C lower in the case of LCR and LMM leather–PVC mixtures and to about 20 °C lower for LAY–PVC mixture as expected based on their calculated curves. The maximal mass loss rates were measured at 301 °C for both LCR–PVC mixtures (Figs. 1d and 1j), at 308 °C for both LAY–PVC mixtures (Figs. 1e and 1k), and at 296–297 °C for LMM–PVC mixtures (Figs. 1f and 1l). Surprisingly, the temperatures of maximal mass loss rates of the mixtures were the same regardless of the mixing ratio.

The TG/MS curves of PVC and its mixtures with LMM (Fig. 2b–d)

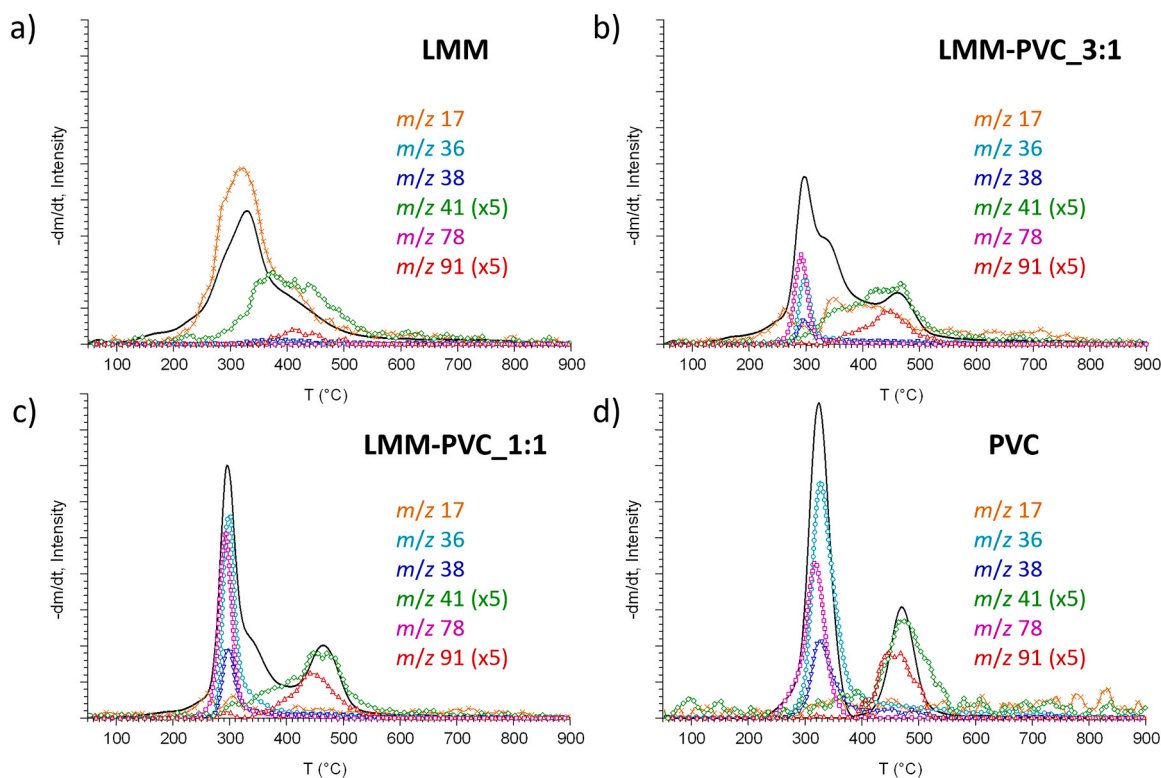


Fig. 2. DTG and some ion intensity curves of (a) LMM, (b) LMM-PVC_3:1, (c) LMM-PVC_1:1 and (d) PVC samples. The ion intensity curves with different scales are indicated with a scale factor. The scale of the ion intensity curves is the same between the subfigures. The DTG and some ion intensity curves of the LCR, LAY and their PVC mixtures can be found in the [Supplementary material](#) (Figs. S1–S2).

show that hydrogen chloride (m/z 36 and m/z 38) evolved in the first decomposition step of the mixtures at around 300 °C, which can be attributed to dehydrochlorination of the PVC component. Simultaneously, the residual polyene segments undergo cyclization accompanied by chain cleavages resulting in the release of mainly benzene (m/z 78). The TG/MS results of the LCR-PVC and LAY-PVC mixtures can be found in the [Supplementary material](#) (Figs. S1–S2). It was established earlier that the presence of specific metal oxides, e.g., chromium(III) oxide, iron(III) oxide, titanium dioxide modified the thermal decomposition of PVC and shifted the dehydrochlorination step to lower temperatures [47,48]. While the catalytic effect of chromium may contribute to the changes observed in the cases of LCR-PVC mixtures, due to the chromium(III) content of LCR, chromium cannot be the only factor. Catalyzed dehydrochlorination was also detected during the decomposition of mixtures with the other types of leathers (i.e., LAY and LMM), where the dehydrochlorination was similarly shifted to significantly lower temperatures as mentioned above. These results suggest that, in addition to the catalytic effect of the metal content, the leather matrix itself plays a role in PVC decomposition. The enhanced dehydrochlorination can be explained by the basic properties of the protein chains present in the leather, which catalyze the elimination of hydrogen chloride from PVC. A similar effect was observed in the case of thermal decomposition of synthetic polyamide-PVC mixtures, where the dehydrochlorination step of PVC also shifted to lower temperatures [49]. The same study revealed that the presence of some non-basic polymers such as PP, PS, polyisoprene and PMMA does not significantly affect the dehydrochlorination step of PVC. Samart and Duangchan [50] reported the results of the co-pyrolysis measurements of PVC and cattle manure. They found that cattle manure provided a large amount of basic nitrogen compounds, which reacted with hydrogen chloride. They established that biomass rich in basic nitrogen compounds was beneficial for reducing hydrogen chloride emission. The efficiency of hydrogen chloride removal at 450 °C increased from 40 %

to 80–85 % by amount of substance, when the amount of nitrogen compounds increased in the mixture. Therefore, the main decomposition products of collagen (i.e., ammonia and nitrogen-containing DKPs) can also facilitate the dehydrochlorination step of PVC in the PVC-leather mixtures.

Based on the ion intensity curves of m/z 78 indicating benzene evolution, the onset temperature of PVC decomposition was at around 230 °C in the cases of each sample, similar for all leather-PVC mixtures regardless of the tanning type and for pure PVC, as well. However, the dehydrochlorination of PVC reached its maximal rate at lower temperatures and occurred within a narrower temperature range in the presence of leather. These observations also prove that the basic environment provided by the polypeptide chains of leather facilitated the dehydrochlorination process of PVC.

Ammonia (m/z 17) was a major decomposition product of leather and evolved between 250 and 500 °C (Fig. 2a). The comparison of the intensity curves of hydrogen chloride (m/z 36 and 38) and ammonia (m/z 17) confirms the significant interaction between the components within the mixtures. Highly reduced amount of ammonia evolved from the mixtures (Fig. 2b–c). Moreover, the amount of detected hydrogen chloride also decreased in the mixtures, which can be observed in the ratio of the intensities of the hydrogen chloride (m/z 36 and 38) and benzene (m/z 78) ion curves, as both compounds form exclusively and simultaneously from PVC during its first decomposition step. Hydrogen chloride (m/z 36 and 38) curves were measured about one and a half times higher than the maximal intensity of benzene in the case of the pure PVC sample (Fig. 2d), but their ratio was measured similar or lower from mixtures with 1:1 ratio (Fig. 2c). In the cases of mixtures with 3:1 sample, the maximal intensity of hydrogen chloride was much lower than the maximal intensity of benzene (Fig. 2b). The decreased release of these compounds suggests that the formation of other decomposition products was more favorable. In addition, a gas phase reaction between free ammonia and hydrogen chloride probably occurred, forming

ammonium chloride, which was not detected by the MS.

The thermal decomposition step of the mixtures between 400 and 520 °C is related to the second decomposition step of the PVC component and carbonization of the leather, which is additionally confirmed by the peaks of the fragment signals at m/z 41 and 91 in this temperature range as presented in Fig. 2. The curves of m/z 41 can be attributed to propenyl fragments from both components and to acetonitrile from leather [29]. The ion curves at m/z 91 indicate toluene and other compounds decomposing into benzyl fragments in the MS. As Fig. 2 demonstrates, they are formed mostly from PVC, but leather also produces some alkylated aromatic compounds.

3.3. Py-GC/MS analysis of the samples

3.3.1. Characteristic decomposition products

Py-GC/MS measurements were carried out to identify the main volatile decomposition products of leather samples, PVC and their mixtures at different ratios. The pyrolysis temperature was set at 500 °C based on the TG/MS measurements, as these indicated that the main thermal decomposition steps are completed at this temperature, ensuring complete analysis of the sample's volatile profile. The pyrograms of LMM, PVC and their mixtures are shown in Fig. 3, and the identified decomposition products are listed in Table 3. The pyrograms of the LCR-PVC and LAY-PVC mixtures can be found in the [Supplementary material](#) (Figs. S3–S4). The characteristic decomposition products of both leather [e.g., carbon dioxide (peak #1), acetonitrile

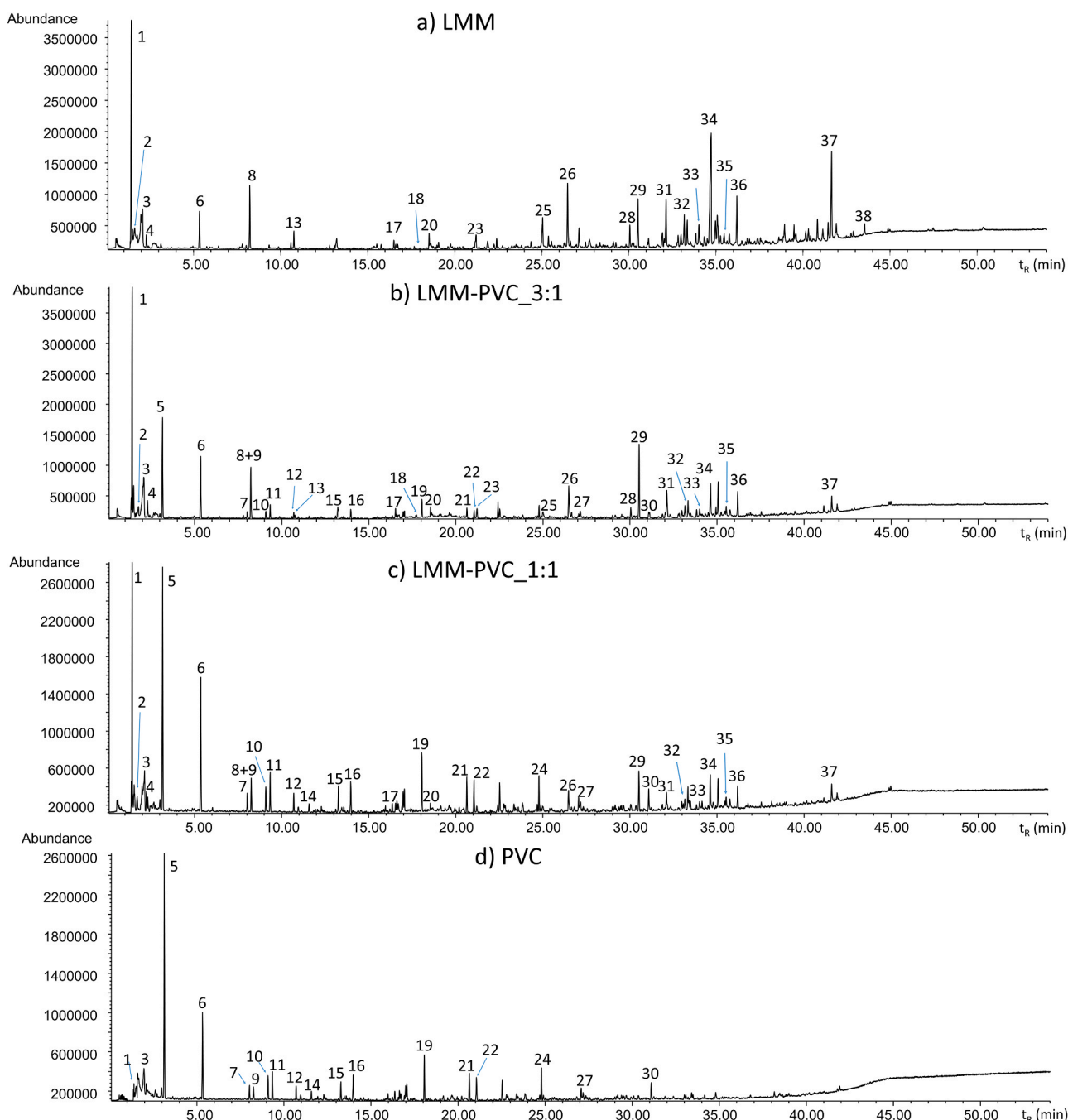


Fig. 3. Pyrograms of (a) LMM, (b) LMM-PVC_3:1, (c) LMM-PVC_1:1 and (d) PVC. The identification of the peaks is given in Table 3.

Table 3

The main decomposition products identified in the Py-GC/MS measurements of LMM, PVC and their mixtures. The numbers in the first column refer to the peaks in Fig. 3.

No.	Ret. time (min)	Compounds	Characteristic <i>m/z</i> values
1	1.42	Carbon dioxide + chloromethane	44 + 50,52
2	1.77	Hydrogen cyanide	27,26
3	2.07	Water	18,17
4	2.29	Acetonitrile	41,40,37
5	3.13	Benzene	78,77,52
6	5.34	Toluene	91,92,65
7	8.02	Ethylbenzene	91,106,77
8	8.23	Pyrrole	67,41,39
9	8.25	Xylene	91,106,105
10	9.09	Xylene	91,106,105
11	9.34	Styrene	104,103,78
12	10.70	C ₃ -benzene isomers	117,91,118 + 91,120,65
13	10.76	2-Methylpyrrole	80,81,53
14	11.58	C ₃ -benzene isomer	105,120,91
15	13.27	Propenylbenzene	117,118,115
16	13.98	Indene	115,116,89
17	16.54	Phenol	94,66,65
18	17.71	<i>o</i> -Cresol	108,107,79
19	18.06	Naphthalene	128,127,129
20	18.53	<i>p</i> -Cresol	107,108,77
21	20.65	Methylnaphthalene	142,141,115
22	21.06	Methylnaphthalene	142,141,115
23	21.23	Succinimide	99,56,42
24	24.79	2,6-Di- <i>tert</i> -butyl-4-methylphenol	205,220,145
25	25.05	Pyrrole-2-carboxamide	110,94,93
26	26.48	Resorcinol	110,82,81
27	27.07	Fluorene	165,166,83
28	30.06	Pyrazine derivative	136,107,108
29	30.52	Pyrocoll	186,93,65
30	31.10	Phenanthrene	178,176,179
31	32.14	Unidentified compounds	94,164,93 + 171,172
32	33.18	Proline-alanine DKP (isomer 1)	70,168,97
33	34.02	Proline-alanine DKP (isomer 2)	70,168,97
34	34.72	Proline-glycine DKP	83,111,154
35	35.47	Proline-dehydropyrroline DKP	191,192,70
36	36.21	Proline-proline DKP	70,194,67
37	41.67	Proline-hydroxyproline DKP	70,210,86
38	43.53	Proline-pyrroglutamine DKP	70,208,96

(peak #4), pyrrole (peak #8), 2-methylpyrrole (peak #13), succinimide (peak #23), pyrrole-2-carboxamide (peak #25), pyrocoll (peak #29) and DKPs (peaks #32–38)] and PVC [e.g., benzene (peak #5), other monoaromatic (peaks #6–7, #9–12, #14–15) and polyaromatic hydrocarbons (PAHs, peaks #16, #19, #21–22, #27, #30)] are present in the pyrolyzates of the leather–PVC mixtures. The peak of resorcinol (peak #26) is remarkable in the pyrograms of LMM and its mixtures (Fig. 3a–c) because resorcinol is a specific decomposition product of the condensed-type vegetable tannins, such as mimosa [11]. Resorcinol was not significant in the pyrolyzate of LAY and its mixtures, as myrobalan is a hydrolysable vegetable tannin. It should be noted that 2,6-di-*tert*-butyl-4-methylphenol (peak #24), a common antioxidant additive, appears in the pyrograms of PVC and its mixtures. The peak integral data of the evaluated compounds are presented in Table S2 of the Supplementary material.

3.3.2. Evolution of leather-derived pyrolysis products from leather–PVC mixtures

The Py-GC/MS measurements provided more details about the changes of leather decomposition when pyrolyzing it in mixtures with PVC. The evaluated intensity data of the identified decomposition products presented below were normalized i.e., calculated per unit mass of leather for comparison. The main decomposition products of leather

itself are DKPs of glycine, alanine, proline, and hydroxyproline, the four most abundant amino acids in collagen, which gives the most part of leather [51–53]. The measured intensities of the most important DKPs are shown in Fig. 4. The results show that the formation of proline-glycine (peak #34) and proline-hydroxyproline (peak #37) DKPs were significantly hindered in the presence of PVC, especially in the cases of 1:1 mixtures. Fig. 4 also presents the normalized intensities of proline-proline (peak #36), two isomers of proline-alanine (peaks #32 and #33) and proline-dehydropyrroline DKPs (peak #35). In general, the relative intensities of these DKPs were reduced to a lesser extent in the cases of mixtures than the intensities of the two main DKPs. However, the decrease was apparent in the measurement of LAY–PVC_1:1.

The formation of smaller decomposition products of leather also showed some changes when leather was pyrolyzed in a mixture with PVC. For example, the relative intensities of two nitriles, i.e., hydrogen cyanide and acetonitrile (methyl cyanide), formed by the fragmentation of collagen [29], showed an increase in the presence of the PVC. As for hydrogen cyanide, this phenomenon was obvious in most cases regardless of the leather type and mixture ratio. The formation of hydrogen cyanide at least tripled in the case of the LMM–PVC mixtures. On the other hand, the increase in acetonitrile evolution was rather moderate in the presence of PVC. The results show that the presence of PVC hindered the formation of the most common DKPs (Fig. 4), while the fragmentation of collagen was promoted during the pyrolysis of leather–PVC mixtures (Fig. 5).

The normalized relative intensities of phenolic decomposition products are shown in Fig. 6. The results indicate that the effect of PVC is ambiguous on the evolution of these oxygenated compounds. However, the extent of formation of phenols depended more on the tanning type of leather than on the effect of PVC during co-pyrolysis. It should be noted that LCR and its mixtures released significantly more phenols, especially *o*-cresol (Fig. 6b), than the samples containing LAY or LMM. This suggests a catalytic influence from a component unique to LCR or present at higher concentration in LCR. Chromium occurs only in LCR, and its sulfur content is approximately three times greater than that of the other two leather samples. Therefore, both chromium and sulfur are potential promoters of the formation of more phenol and cresols from LCR during pyrolysis. However, taking into consideration the chemical nature of the two moieties, the catalytic effect of chromium is more plausible.

3.3.3. Evolution of aromatic hydrocarbons from leather–PVC mixtures

In the cases of leather–PVC mixtures, the decomposition products like monoaromatic hydrocarbons may form from both mixture components; therefore, a different approach was applied to evaluate the Py-GC/MS data of these compounds for the comparison of the samples. The synergistic effect of leather and PVC on the formation of benzene, toluene and styrene is revealed by the comparison of the measured relative intensities of the mixtures with the calculated data from the measurements of the individual components summed in a proper ratio. The measured and calculated values in Fig. 7 show that the evolution of benzene, toluene and styrene increased to a small extent in all cases. The amount of the released monoaromatic compounds was higher from 1:1 mixtures than from 3:1 mixtures, reflecting that PVC produces a higher proportion of these compounds. The only exception is styrene formation from LCR–PVC mixtures, where samples released more styrene than the other leather–PVC mixtures, while both the measured and the calculated values were similar despite of the different mixing ratios (Fig. 7c). The reason for this observation is that similar amounts of styrene evolved during the decomposition of PVC and LCR. Unlike the other leather samples, LCR had a thin artificial polystyrene coating on its surface, which depolymerized during pyrolysis and contributed to the increased styrene formation.

Highlighting these findings, the increased monoaromatic formation in these mixtures may prompt the consideration of alternative binders or additives in product design to enhance safety and environmental performance. This forward-looking approach could help guide the

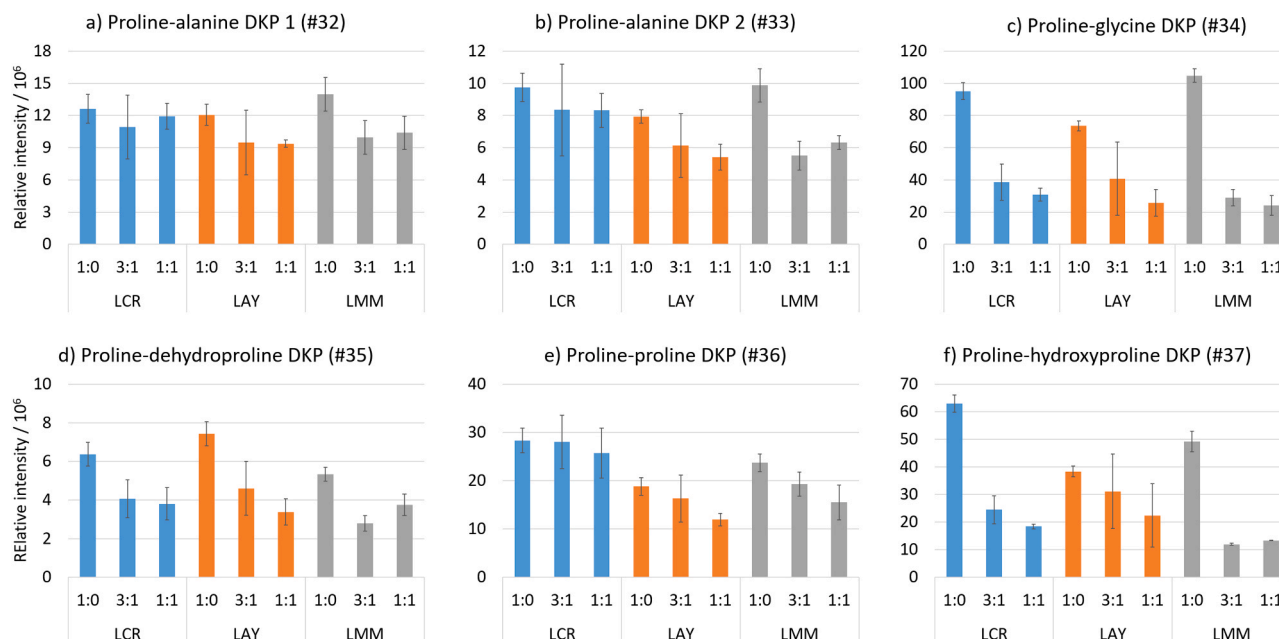


Fig. 4. The relative intensities of some DKPs, including (a) proline-alanine 1, (b) proline-alanine 2, (c) proline-glycine, (d) proline-dehydroproline, (e) proline-proline, and (f) proline-hydroxyproline DKPs, evolved during the pyrolysis of leather samples (marked by 1:0) and leather-PVC mixtures (3:1 and 1:1).

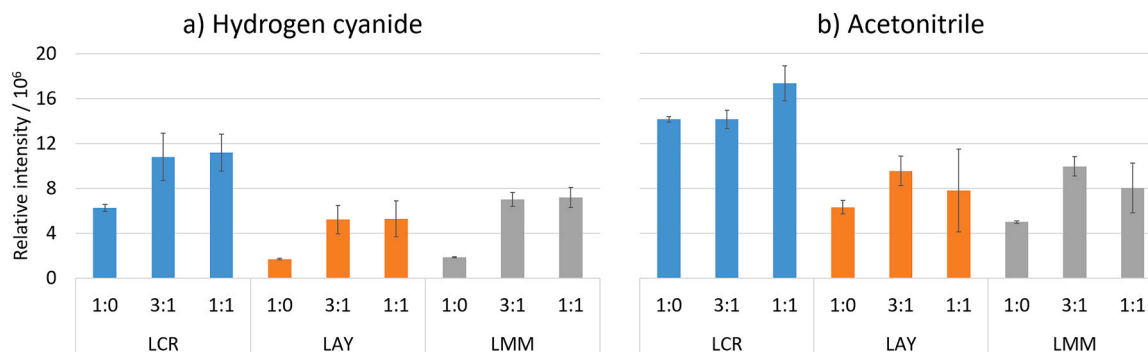


Fig. 5. The relative intensities of (a) hydrogen cyanide and (b) acetonitrile evolved during the pyrolysis of leather samples and leather-PVC mixtures.

development of leather-PVC composites with reduced aromatic emissions.

The relative intensity data in Fig. 8 present the extent of PAH formation detected in the Py-GC/MS measurements of PVC and its mixtures with different leather samples. PVC can be considered the main source of PAHs as only traces of PAH compounds were detected from the tanned leathers. Therefore, for a simpler comparison, the relative intensity values for the mixtures were calculated per unit mass of PVC. The results show that in most cases, the presence of leather as a mixture component slightly increased the formation of different PAH compounds, the source of which was mainly the advanced thermal decomposition of PVC. The slightly increased formation of PAHs and monoaromatic compounds could explain the slightly decreased amounts of char from the mixtures as it was measured by TGA (Fig. 1). While this increase in PAH emissions was modest, it is important to assess its potential impact in real-world scenarios. For instance, even a slight rise in PAHs could have implications for emission thresholds set by environmental regulations, emphasizing the need for further investigation into the sustainability and environmental impact of these materials in practical applications.

3.3.4. Evolution of chloromethane from leather-PVC mixtures

Besides hydrogen chloride, the evolution of chloromethane as a chlorine-containing compound was detected during the pyrolysis of the

leather-PVC mixtures. The relative intensities measured in the mixtures are presented in Fig. 9. The results show that more chloromethane formed from the 3:1 mixtures than from the 1:1 mixtures regardless of the tanning type of the leather component. It should be noted that the signal of chloromethane was under the detection limit from each leather sample and PVC during the Py-GC/MS measurements. Therefore, in the cases of the mixtures, the methyl part of chloromethane probably originated from leather decomposition, while chlorine derived from PVC.

It is noteworthy that traces of chlorobenzene were released, but no other chlorinated aromatic compounds were detected among the decomposition products of leather-PVC mixtures. Despite the interaction of the components discussed above, the intensity of chlorobenzene was not larger from any kind of leather-PVC mixtures than from PVC, similarly to the co-pyrolysis of PVC with other biomass-related materials [54].

3.3.5. Modeling the effect of hydrogen chloride evolution on the pyrolysis of leather

The role of hydrogen chloride formed by the dehydrochlorination of PVC in the thermal decomposition of leather-PVC mixtures was further investigated. For this aim, leather samples treated with hydrochloric acid solution were pyrolyzed to reveal the specific effect of hydrogen chloride on leather thermal degradation during the pyrolysis of

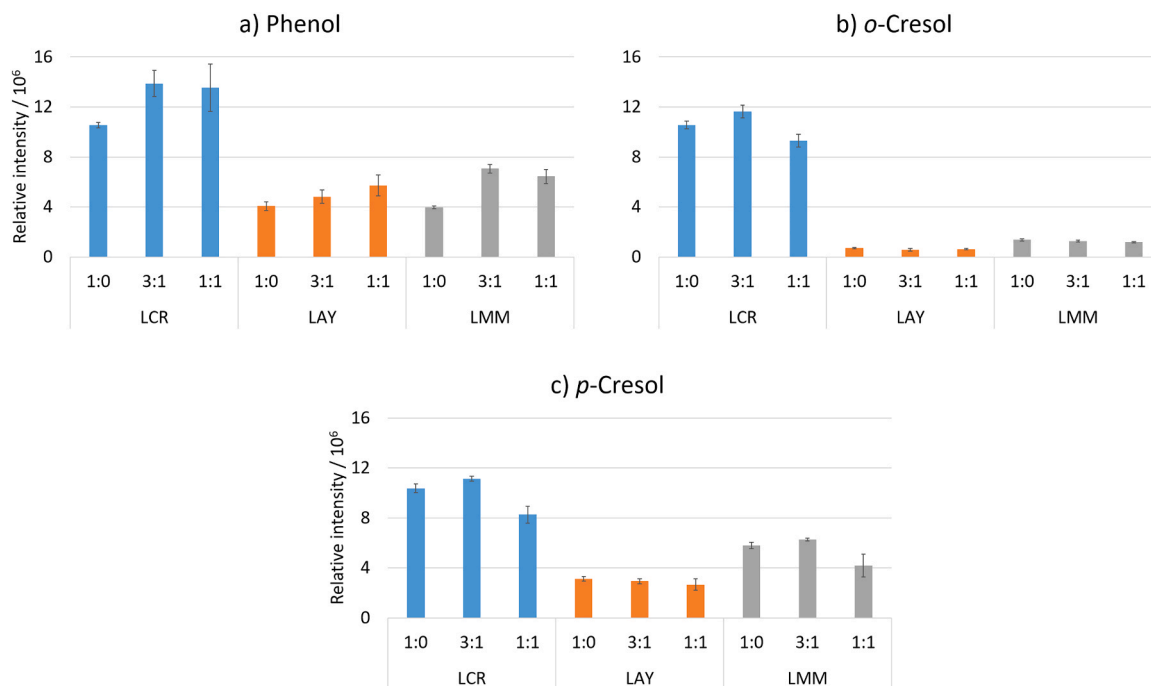


Fig. 6. The relative intensities of some phenolic compounds, including (a) phenol, (b) *o*-cresol and (c) *p*-cresol, evolved during the pyrolysis of leather samples and leather-PVC mixtures.

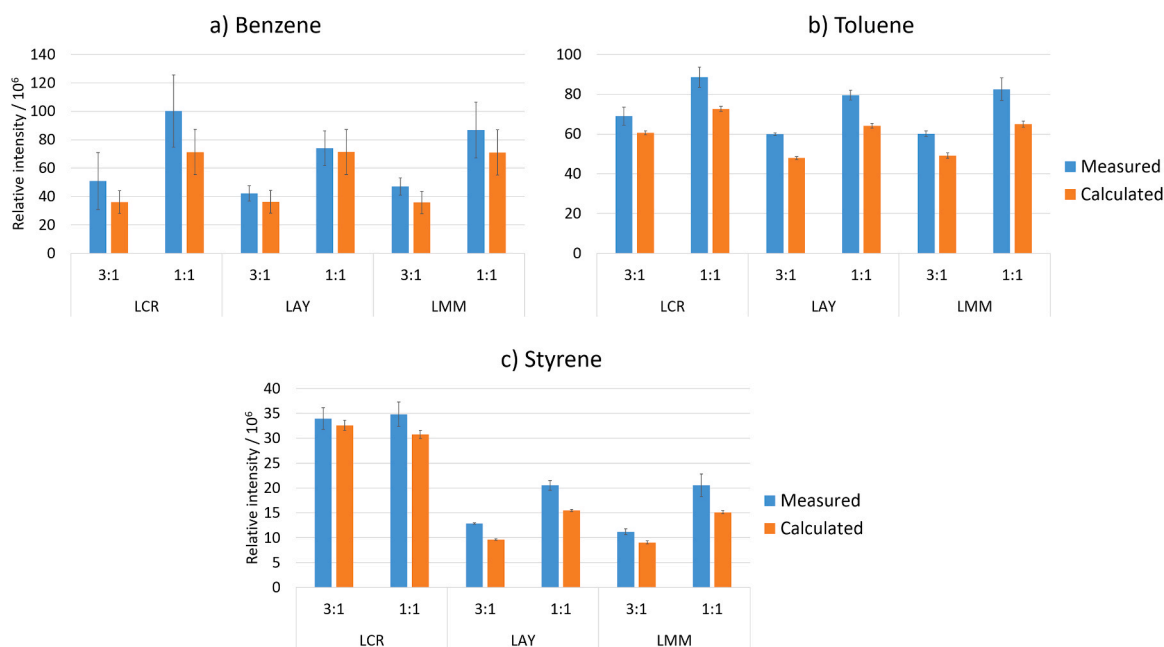


Fig. 7. The calculated and measured relative intensities of (a) benzene, (b) toluene and (c) styrene evolved during the pyrolysis of leather-PVC mixtures.

leather-PVC mixtures. The mass ratio of hydrogen chloride added in solution to the leather and the sample preparation procedure is detailed in Section 2.2.3. Among the leather samples, LMM was selected for these Py-GC/MS experiments.

Fig. 10a demonstrates that the presence of hydrogen chloride in the LMM+HCl sample increased the formation of hydrogen cyanide and acetonitrile to a similar extent as the PVC-derived hydrogen chloride evolution in the cases of the LMM-PVC mixtures (Fig. 5) in comparison to the LMM sample. Therefore, we can confirm that hydrogen chloride from the decomposing PVC is likely the primary promoter of the increased formation of hydrogen cyanide and acetonitrile during the

pyrolysis of the leather-PVC mixtures. The relative intensities of the two most abundant DKPs (i.e., proline-glycine and proline-hydroxyproline) decreased in the presence of hydrogen chloride, while the amount of minor DKPs changed within the standard deviation of the method (Fig. 10b). Notably, the extent of DKP suppression was more pronounced in the leather-PVC mixtures for all DKPs (Fig. 4) than in the LMM+HCl sample (Fig. 10b). This suggests that in addition to the effect of hydrogen chloride in the cases of leather-PVC mixtures, the presence of the PVC residue, namely the remained polyene chains may further hinder the decomposition of the polypeptide chains of leather into cyclic dimers, i. e. DKPs.

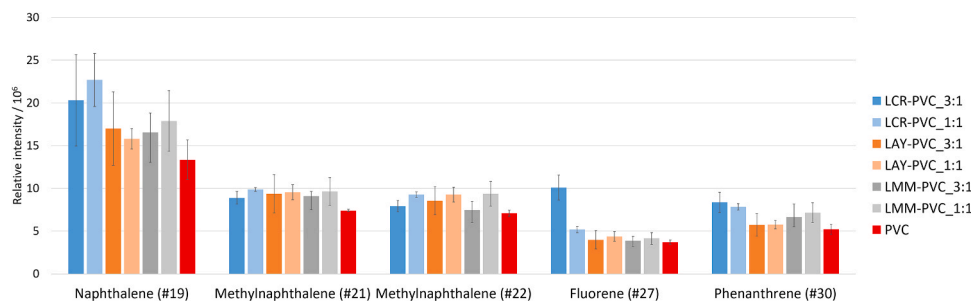


Fig. 8. The relative intensities of some PAHs evolved during the pyrolysis of PVC and leather-PVC mixtures.

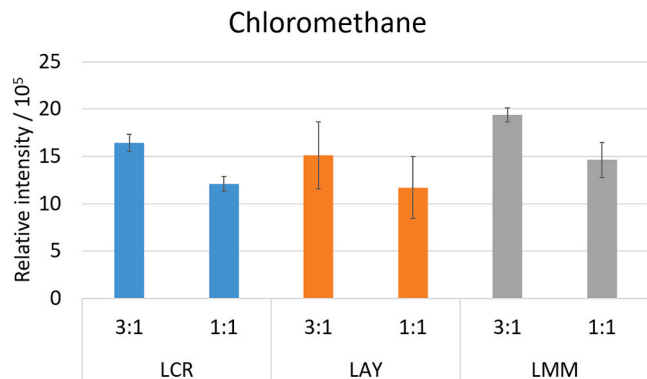


Fig. 9. The relative intensities of chloromethane evolved during the pyrolysis of leather-PVC mixtures.

3.3.6. Thermal decomposition routes in leather-PVC mixtures

The complex reaction mechanisms of the main macromolecules of the leather-PVC mixtures, i.e., collagen and PVC, are illustrated in Fig. 11. Proteins decompose mostly by three types of reaction during pyrolysis. Depolymerization of the protein chains results in the formation of cyclic dimers, i.e., diketopiperazines (DKP). Fragmentation of the amide units leads to the release of several nitrogen-containing molecules, such as NH_3 , HCN , CH_3CN , HNCO , and to the formation of CO , CO_2 and H_2O . Aliphatic fragments can be formed mostly from the proline and hydroxyproline amino acid residues of collagen. The formation of toluene illustrates the third type of reaction: scission of the side-groups. The thermal decomposition of PVC occurs in two main steps. Dehydrochlorination leaves behind ideally polyacetylene chains, which decompose by the formation of benzene. However, the irregular structures (e.g., a crosslink shown in Fig. 11) are also present in the decomposing polymer, which are responsible for the formation of alkyl- and alkenylbenzenes during the second stage of PVC decomposition.

Most of the decomposition products of the mixtures are the same as those of the individual protein and PVC. The intensity changes of the most significant volatile products observed during the co-pyrolysis of

leather and PVC are indicated by arrows in Fig. 11. As discussed above, PVC enhanced the fragmentation of collagen chains and hindered the depolymerization to DKPs. On the other hand, leather promoted the release of aromatic compounds accompanied by the decrease of carbonaceous residue. Methyl chloride is formed only from the leather-PVC mixtures indicating the reaction between alkyl fragments of protein chains and chlorine content of PVC. The formation of NH_4Cl (not detectable by our methods) might contribute to the reduction of NH_3 and HCl .

4. Conclusion

The thermal decomposition of leather-PVC mixtures was studied using TG/MS and Py-GC/MS. The results show that mixing alters the thermal decomposition of both leather and PVC.

The most significant difference between the measured and calculated TG curves of the mixtures was the shift of the first decomposition step of PVC to lower temperatures. The shift occurred regardless of the type of leather or the mixing ratios. The evolution curves of hydrogen chloride measured by TG/MS also confirmed the reduced thermal stability of PVC in the presence of leather. The basic environment provided by the polypeptide leather facilitated the dehydrochlorination step of PVC. As a result, this step shifted to lower temperatures by 20–30 °C. The amount of carbonaceous products remaining after the complete degradation of the mixtures also decreased.

Detailed analysis of the released volatile decomposition products detected by Py-GC/MS shows that the presence of PVC promotes fragmentation reactions of the polypeptide chains at the expense of depolymerization within the leather part of the mixtures. The formation of small molecules like hydrogen cyanide and acetonitrile was more pronounced, while the formation of cyclic dipeptides (DKPs) from leather was hindered in the presence of PVC. Increased yields of mono- and polyaromatic hydrocarbons were also detected from the leather-PVC mixtures, which could contribute to the decreased char yields of the mixtures.

The effect of PVC-originated hydrogen chloride on the thermal decomposition of leather during the co-pyrolysis was verified by measuring a model sample LMM+HCl. It was confirmed that hydrogen

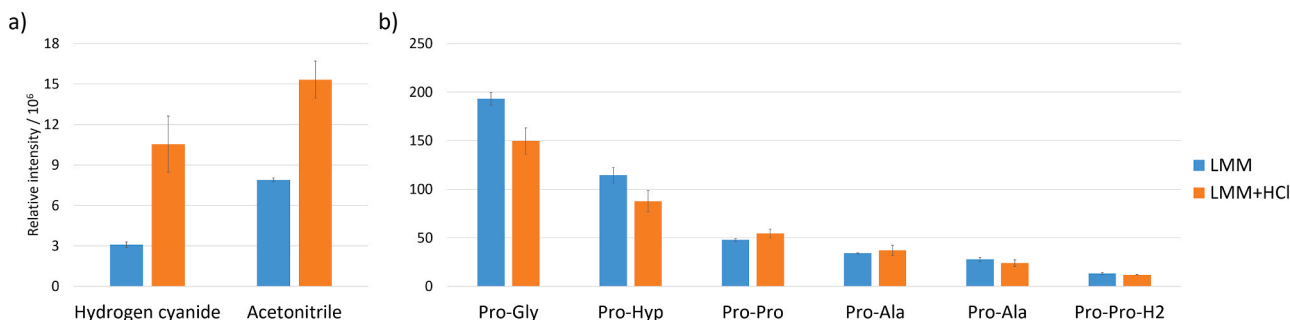


Fig. 10. The relative intensities of (a) hydrogen cyanide, acetonitrile, and (b) some DKPs evolved during the pyrolysis of LMM and LMM+HCl samples.

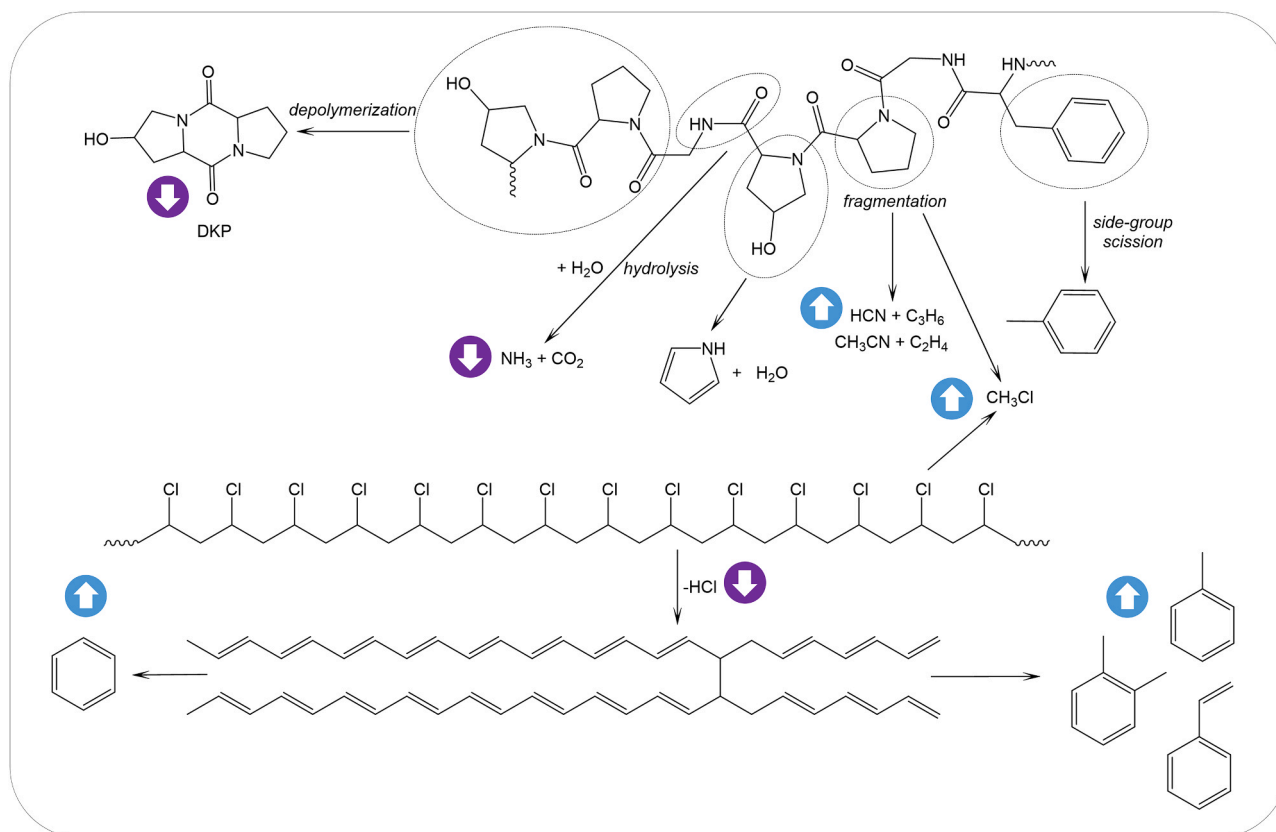


Fig. 11. Proposed decomposition routes of leather-PVC mixtures and synergistic effects observed during co-pyrolysis.

chloride was the primary promoter of enhanced hydrogen cyanide and acetonitrile formation from leather-PVC mixtures.

Finally, though the formation of chloromethane was detected in the pyrolyzate of the leather-PVC mixtures, no additional chlorinated organic compounds were formed as a result of interactions between the components.

CRedit authorship contribution statement

István Sándor Czírok: Writing – original draft, Visualization, Investigation, Data curation. **Zoltán Sebestyén:** Writing – review & editing, Visualization, Supervision, Funding acquisition. **Bence Babinszki:** Writing – original draft. **Elena Badea:** Writing – review & editing. **Emma Jakab:** Writing – review & editing. **Zsuzsanna Czégény:** Writing – review & editing, Supervision, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jaap.2025.107558](https://doi.org/10.1016/j.jaap.2025.107558).

Data availability

Data will be made available on request.

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