

Research Article

Impact of Leather on the Fire Resistance of Leather-Wood Fibreboard: FT-IR Spectroscopy and Pyrolysis-GC-MS Investigation

T. Schnabel ¹, M.-C. Barbu,^{1,2} E. Windeisen-Holzhauser,³ A. Petutschnigg ^{1,4}
and G. Tondi ^{1,5}

¹Department of Forest Products Technology and Timber Constructions, Salzburg University of Applied Sciences, Markt 136a, 5431 Kuchl, Austria

²Faculty of Wood Engineering, “Transilvania” University of Brasov, Faculty of Wood Engineering, Str. Universitatii nr.1, 500068 Brasov, Romania

³Holzforschung München, Technische Universität München, Winzererstraße 45, 80797 München, Germany

⁴BOKU University of Natural Resources and Life Sciences, Konrad Lorenzstraße 24, 3430 Tulln, Austria

⁵CNR-IVALSA Via Madonna del Piano 10, 50019 Sesto Fiorentino, FI, Italy

Correspondence should be addressed to T. Schnabel; thomas.schnabel@fh-salzburg.ac.at and G. Tondi; gianluca.tondi@fh-salzburg.ac.at

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Leather-wood fibreboards are innovative composite materials, which combine together the high mechanical properties of wood with the superior fire behaviour properties of leather. This study deals with the understanding of the combustion mechanism of the wet-white leather panel. During burning, an overlay coating-like surface is formed on top of a foamy structure that creates the heat transfer barrier. The FT-IR spectroscopy results of the leather show the rearrangement of the proteins and the formation of an increasing amount of acid groups when the exposure to hot gun at over 530°C was prolonged. These acid moieties can react with amino groups of other peptide chains, building a protective polymer network which hinders the oxygen to reach the core of the panel. Simultaneously, the gases produced during rearrangement cannot easily leave the material, producing a foamy structure which slows down the heat transfer to the core of the material. The Py-GC-MS analysis shows that the gases produced by the wet-white leather-type protein-based boards were amino-aromatic compounds like the diketopiperazine (DKP), which do not burn easily. The combination of the effects of (i) formation of the overlay coating-like surface, (ii) establishment of the foamy structure, and (iii) degassing of DKP explains the outstanding fire properties of leather and wood-leather fibreboards.

1. Introduction

Wood and leather are two of the oldest human civilization-used natural raw materials. Based on their organic compositions, their fire resistance is expected to be low. Particular wood fibreboards like medium-density fibreboard (MDF) are usually prone to fire hazard [1–3]). However, the combination of wood and leather changes the properties of both bioresources, resulting in improved composite material [4]. The reasons of this behaviour and the chemical reactions involved are unexplained.

In leather, at least twelve collagen types can be distinguished; however, type I is the most common and contains 32.4% glycine, 12.2% proline, 9.8% alanine, 9.8% hydroxyproline, 7.2% glutamic acid, 4.4% aspartic acid, 4.8% arginine, 4.0% between leucine, and isoleucine and minor amount of the other aminoacids such as serine, lysine, and valine (2 to 3% each) [5–9]. The tanning process can occur in three chemical ways: (i) through covalent bonds; (ii) through coordination bonds, and (iii) through secondary forces such as hydrogen bonds [6], and it generally affects the hydrothermal stabilization and the denaturation temperature of

collagen [10]. Different viewing angles about fire resistance properties of leather were found in the literature: On the one hand, several studies showed the need for additional flame retardant in order to meet the safety requirements of the market [11–13]. On the other hand, some publications presented leather has a naturally fire-resistant material [14–16], whereas the chemical process occurring was not elucidated.

Mixed panels of wood fibre and leather shavings are innovative and sustainable composites which combine the high mechanical properties of wood with the high fire resistance of leather [17]. A broad set of fibreboards with different amounts of leather and wood were tested to analyze the influence of the leather on mechanical strengths (e.g., bending strength and internal bond) [18–20]. Chemical characterization of these products was also performed with several techniques like ^{13}C -NMR, Raman, FT-IR, and FT-NIR spectroscopy [21–24]. These studies have allowed to identify the interaction between the components of the leather-wood fibre panels which resulted extremely interesting for cladding and ceiling of green buildings but also as inner material for automotive and nautical casing due to their natural/sustainable composition and their high fire resistance.

However, the technological reasons for the improved fire properties observed for leather panels are unknown yet; hence, in the present study, the natural fire resistance of leather was investigated by microscopic analysis, FT-IR spectroscopy, and Py-GC-MS. The chemical changes due to the burning process were observed, and a possible mechanism that contributes to the outstanding fire properties of leather was also proposed.

2. Materials and Methods

2.1. Materials. Residual leather particles of the shaving process of synthetically tanned leather type “wet white” were used. These shavings were sieved and particles smaller than 2 mm were further used and were dried in a kiln at 40°C until the moisture content of $8 \pm 1\%$ was reached.

Industry-refined Norway spruce (*Picea abies*) wood fibres ($l=3\text{--}5\text{ mm}$) for the fibreboards (type MDF) production at moisture content of $8 \pm 1\%$ were used. Urea-formaldehyde (UF) resin with 66% solid content was used for the production of the fibreboards using ammonium sulphate solution (33%) as hardener.

2.2. Fibreboard Manufacturing. Wood fibreboards, leather boards, and leather-wood fibreboards with dimensions $450 \times 450 \times 4.5\text{ mm}^3$ were produced according to the following formulations: (i) 90% spruce fibres, (ii) 90% leather shavings, and (iii) 45% (w/w) spruce fibres and 45% (w/w) leather shavings were glued with 10% urea-formaldehyde resin (UF Prefere 10F102) with 1% ammonium sulphate solution in a lab ploughshare blender type with a two-substance nozzle (Schlick) upright section. The glued fibres were distributed manually in a frame and then pressed in an automated hot lab press (Höfer HLPO 280) at 80°C for

4.5 minutes. These mild hot pressing conditions were used to minimize the degradation of the leather during manufacturing [25]. The panels were then stabilized at 20°C and 65% relative humidity for one week before being characterized.

2.3. Hot-Gun Perforation Test. A wooden frame with heat-protecting gypsum fibreboard was built as a sample holder. In this frame, the $100 \times 100 \times 4.5\text{ mm}^3$ samples were inserted. The hot gun itself was fixed at a distance of 2.5 cm from the panel surface, and the airstream was focused to the centre of the sample. The experimental setup is shown in Figure 1. The samples were exposed to constant airflow of 250 l/min using a hot air blower (Bosch GHG 660 LCD Professional). A constant temperature of 530°C was measured with a thermocouple applied on the panel surface. The time needed to burn through the panels with 4.5 mm thickness was registered as perforation time. The perforation of the fibreboard was defined as the moment at which a visible glowing hole was formed in the backside of the tested panel [25].

2.4. Microscopic Analysis. Samples of the leather panels were observed under the loop of an optical microscope before and after the hot-gun perforation test. The images were acquired with a Nikon Eclipse E200 optical microscope at 10x and 20x magnifications.

2.5. FT-IR Spectroscopy. The slices of leather panel exposed to the hot-gun test for 25 minutes were cut with a scalpel from different area of the heated surface.

The FT-IR spectra were recorded in triplicate between 4000 and 600 cm^{-1} with 32 scans at a resolution of 8 cm^{-1} using a Frontier FT-IR spectrometer (PerkinElmer) equipped with a Miracle diamond ATR accessory with a 1.8 mm round crystal surface. They were successively averaged, baseline corrected, and area normalized with the software the Unscrambler© v. 10.3 (Camo).

2.6. Pyrolysis-GC/MS (Py-GC/MS). Pyrolysis was performed on leather shavings with a Py2020iD double-shot pyrolyzer (Frontier Laboratories) coupled to a 5975C Series GC/MSD system (Agilent Technologies) equipped with a 30 m \times 0.25 mm \times 0.25 μm capillary column (VF-17 ms, Agilent).

Pyrolysis was carried out at 330°C for 0.2 min. The GC program started at 50°C with a heating rate of 5°C/min up to 330°C. At the end of the column, a mass spectrometer allowed to identify the majority of the fractions. In-house library and the NIST 0.8 L databases were exploited for the attribution of the signals of the mass spectra.

3. Results and Discussion

The present study has the objective of understanding the reasons why wood-leather fibreboards showed highly enhanced fire resistance. A comparison between the combustion of wood fibreboard and wood-leather fibreboard is shown in Figure 2.

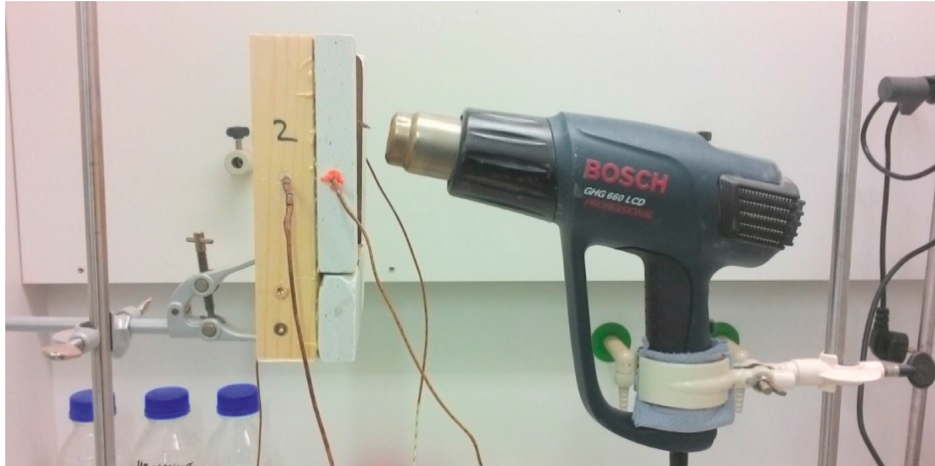


FIGURE 1: Setup of the hot-gun perforation test.

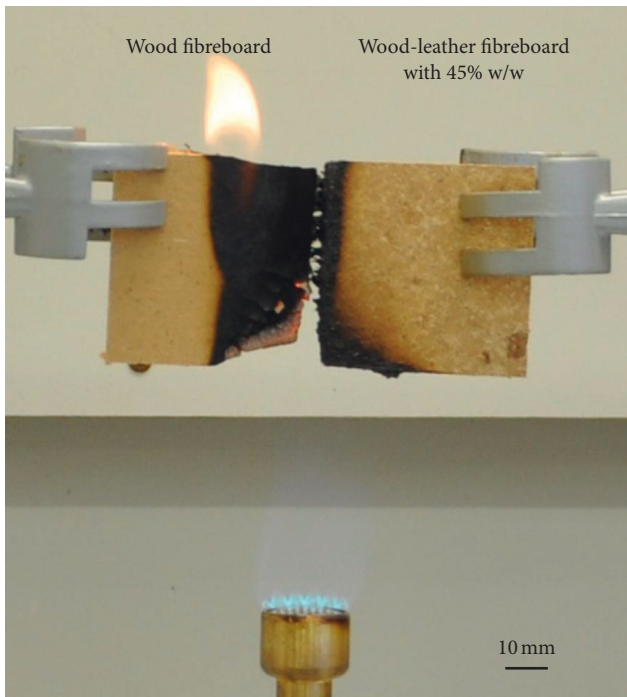


FIGURE 2: Combustion test of wood (left) and wood-leather (right) fibreboards by using a Bunsen burner.

The combustion resistance of wood-leather fibreboards was observed also with the hot-gun perforation test. In this case, wood (90%) fibreboard (MDF), mixed wood (45%)-leather (45%) boards, and pure leather (90%) boards underwent the hot air (530°C) and the time until the 4.5 mm thickness of the boards was burned through were registered according to the method from Rindler [25]. In Figures 3(a)–3(c), the results are reported. The wood fibreboard presented the lower penetration time, and according to the specific density, they needed less than 100 sec to be perforated. The mixed boards presented a set of results which were always much improved from the pure wood product (Figure 3(a)). Finally, the pure leather panel could not be penetrated by the hot-gun energy after

25 minutes, time at which the test was stopped. In the latter experiment, the formation of a black, smooth, and plastic-like surface and simultaneous swelling/foaming behaviour was observed (Figures 3(b) and 3(c)).

These data showed that leather is the major player, and it determines the improved fire resistance of the panels. Therefore, more detailed physical and chemical analyses were done to understand this phenomenon.

3.1. Physical Analysis. The microscopic analysis of the surface of the leather fibreboard after the exposure time of 25 min using the hot-gun test is reported in Figures 4(a) and 4(b).

It can be observed from Figures 4(a) and 4(b) that the surface of the heated leather presents a black, smooth, and plastic-like surface that works as a heat barrier and protect the inner layers for burning. In particular, in Figure 4(a), it can be seen that the surface of the heated part looks shinier and less rough than the unaffected part while in Figure 4(b), a detail of the heated shiny surface is shown. The latter seems to be very tight, and it does not allow the heat to go through.

Further, the swelling of the first layers of material (Figure 3(c)), due to the release of gases (e.g. water, ammonia, nitrogen and carbon oxides), produce a foamy structure which hinders/slows down the heat transfer to the core offering a very effective physical protection against fire.

3.2. Chemical Analysis. FT-IR spectroscopy scans of the leather board after hot-gun exposure were also collected in different positions (Figure 5): unaffected, slightly burned (yellowish region), medium burned (brownish region), and severe burning (black region). Defined trend can be observed, and the major changes observed are the following: the broad band between 3600 and 3100 cm^{-1} as well as the band between 1580 and 1480 cm^{-1} decrease significantly, while two new bands appear at 1770 (only in the severe burning region) and 1720 cm^{-1} (progressively). The band between 3600 and 3100 cm^{-1} is typical for N-H and O-H stretching vibrations. Its decrease is due to two chemical

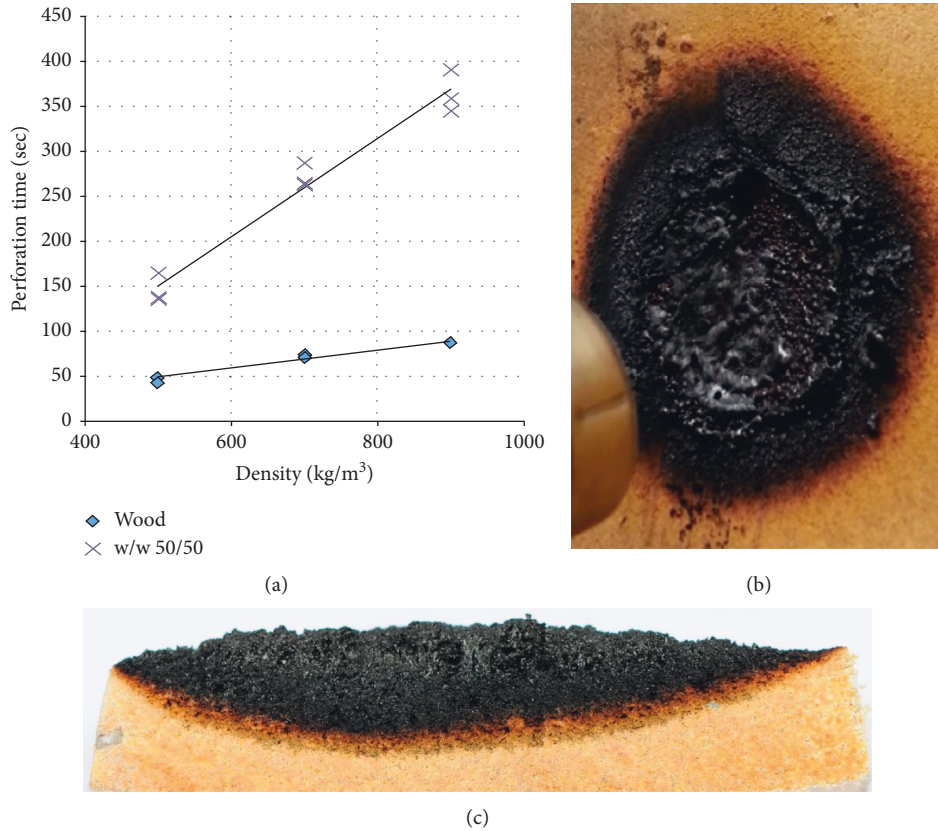


FIGURE 3: Results from the hot-gun perforation test of wood, wood-leather, and leather fibreboards. (a) Perforation time vs density; (b) appearance of the leather surface after 25 minutes of hot-gun exposure; (c) transversal section of the leather (90%) board after 25 minutes of hot-gun exposure.

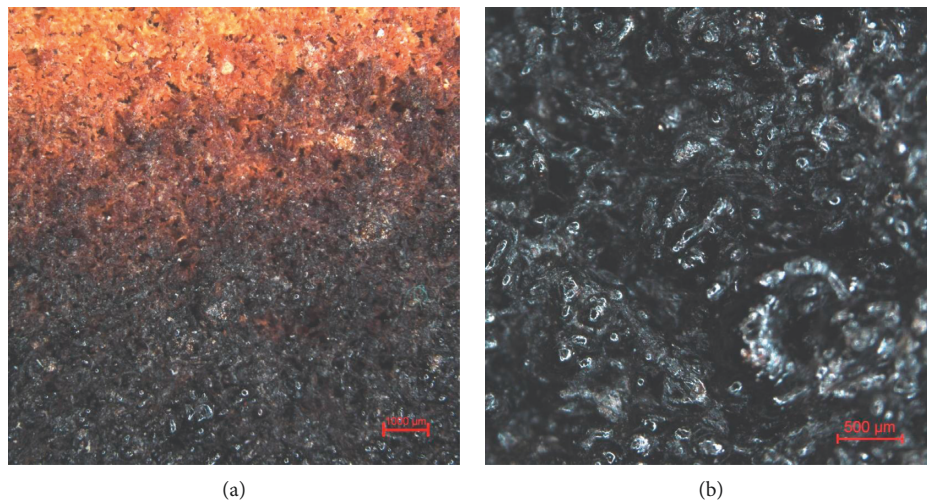


FIGURE 4: Microscopic observation of the surface of leather panels. (a) Border area with 10x magnification; (b) core heated area with 20x magnification.

reactions: (i) the primary and secondary amines evolve to more substituted forms and (ii) alcohols evolve to more oxidized products (e.g., aldehydes and carboxylic acid).

The band at around 1540 cm^{-1} is attributed to out-of-plane vibrations of C-N stretching coupled with N-H bending vibrations (amide II) [26]. This band is affected by establishing

of secondary forces in the secondary structure of the proteins, and its decrease can be attributed to the rupture of this arrangement with formation of random conformations.

The new signals at 1770 cm^{-1} is probably due to the formation of anhydrides after severe burning, while the increasing signal at 1720 cm^{-1} can be attributed to acids [27].

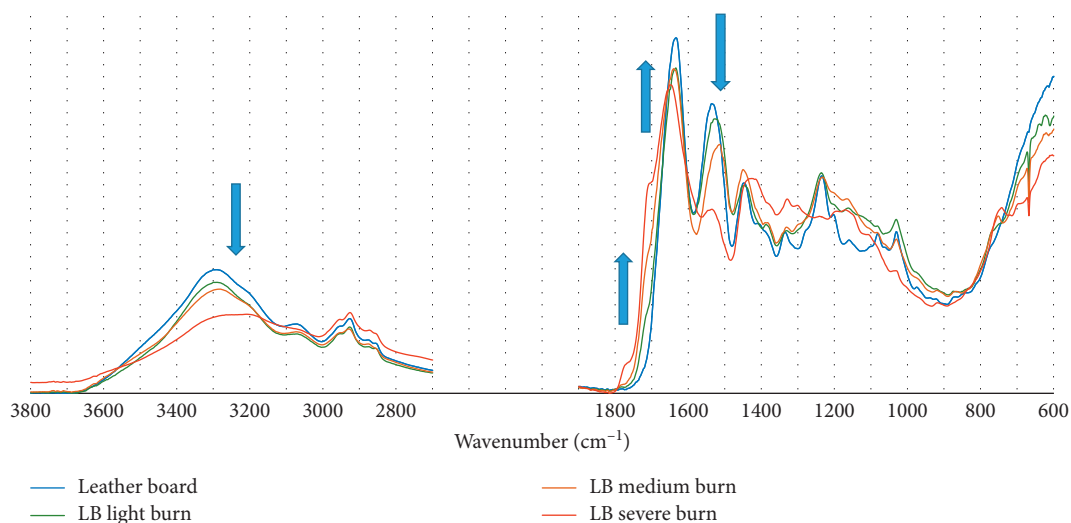


FIGURE 5: FT-IR spectra of “wet-white” leather after hot-gun test in 4 different positions.

This means that during the thermal degradation process, carboxylic groups are formed. The signal at 1720 cm^{-1} band can also be partially attributed to the presence of 2,5-diketopiperazine (DKP) [28] that can be a possible rearrangement for dipeptides [29, 30].

In the schema of Figure 6, a possible rearrangement for a proline-glycine moiety is proposed.

Other milder trends that can be observed are as follows:

(i) the decrease of the signal at 1640 cm^{-1} attributed to the C=O stretching of the amide (amide I) which is the logical consequence of the degradation process because of the amidic bond rupture evolving to more oxidized species (e.g., carboxylic acids and hydroxylamines) and (ii) the band at 1440 cm^{-1} that could be attributed to the presence of higher amount amino-aromatic moieties like pyrazine and pyrrole [28].

These rearrangements begin to be significant when leather is exposed to temperature higher than 250°C for 5 minutes, confirming the findings of previous studies [26].

The thermal degradation of wet-white leather was also observed by pyrolysis-GC/MS at the temperature of 330°C , and the list of the compounds registered is stated in Table 1.

Several fractions were separated during the gas chromatography, and they can be categorized in two families of compounds: (i) nitrogen-containing aromatics, derived by the rearrangement of proteins, and (ii) phenolics, derived from the synthetic tannin used for the tanning of the leather.

The great majority of the molecules released during the GC-MS experiment were nitrogen-containing aromatics (around 75%). These molecules (grey in Table 1) may be produced by the intramolecular cyclization/aromatization of aminoacid pairs and, in particular, the majority of the cases the degradation occurred via simple intra-molecular cyclization of two amino acid units in which one of them was proline. Due to its exceptional conformational rigidity, proline cannot participate to alpha-helix formation [31], and therefore, it constrains the protein chain to assume a folded structure which facilitates the dimeric intramolecular arrangement. The pathway proposed in Figure 6 shows a

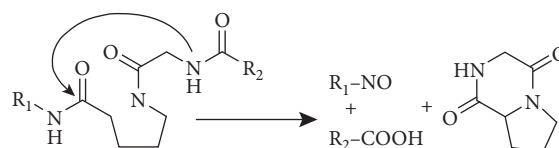


FIGURE 6: Possible reaction schema for the molecular rearrangement of wet-white leather undergoing thermal degradation.

proline-containing protein that cyclizes. This mechanism can occur for many dimers with different branches (Pro-Gly principally, but also Pro-Ala and Pro-Leu which are the three more frequent aminoacids in leather).

So, it results that the degradation of leather is a process that involves the production of several amino-aromatic compounds due to the intramolecular arrangement of the aminoacids under oxidative conditions.

It can be stated that the surface of the leather after thermal degradation results to be (i) richer in acid groups and/or diketopiperazine (DKP) and (ii) poorer of amidic signals and intra-molecular H-bonds due to less organized arrangement. Consistently, the major products of the Py-GC/MS are diketo-nitrogen-containing aromatics.

The findings related to the thermal degradation of wet-white leather shavings boards can be summarized and interpreted as follows:

- (1) During burning, the surface of leather rearranges in an overlay coating-like heat barrier that slows down the penetration of oxygen in the core.
- (2) Simultaneously, the gas developed during burning remains partially blocked into the structure which develops into a foamy structure that delays the heat transmission to the core.
- (3) Leather modifies its structure and rearranges by producing acid moieties.
- (4) These moieties can further react with amino groups of other peptide chains, by producing a networked polymer before undergoing to char. This would be

TABLE 1: Pyrolysis-GC-MS analysis at 330°C of wet-white leather shavings.

Retention time (min)	Assignments	Possible source	Relative amount
20.199	4-Chloro-3-methylphenol	Synthetic tannin	12
23.172	Pyrrole-2-carboxamide	Proline	27
25.871	Xanthine	Glycine	10
26.805	2-Hydroxybiphenyl	Synthetic tannin	29
32.864	Phenol[2,3-e]pyrimidine(1,3,4 H)2-one	Tyrosine	21
34.433/35.117	Hexahydropyrrolo[1,2-a]pyrazine-1,4-dione 2 methyl	Proline + alanine	25/18
36.396	Hexahydropyrrolo[1,2-a]pyrazine-1,4-dione*	Proline + glycine	100
39.065	5,10-Diethoxy-2,3,7,8, tetrahydro-1H,6H-dipyrrolo [1,2-a; 1', 2'-d] pyrazine	Two prolines	32
42.984	Chlorohydroxyl biphenyl	Synthetic tannin	8
44.506	Hexahydro pyrrolo[1,2-a]pyrazine 2-isobutyl-1,4-dione	Proline + leucine or isoleucine	21

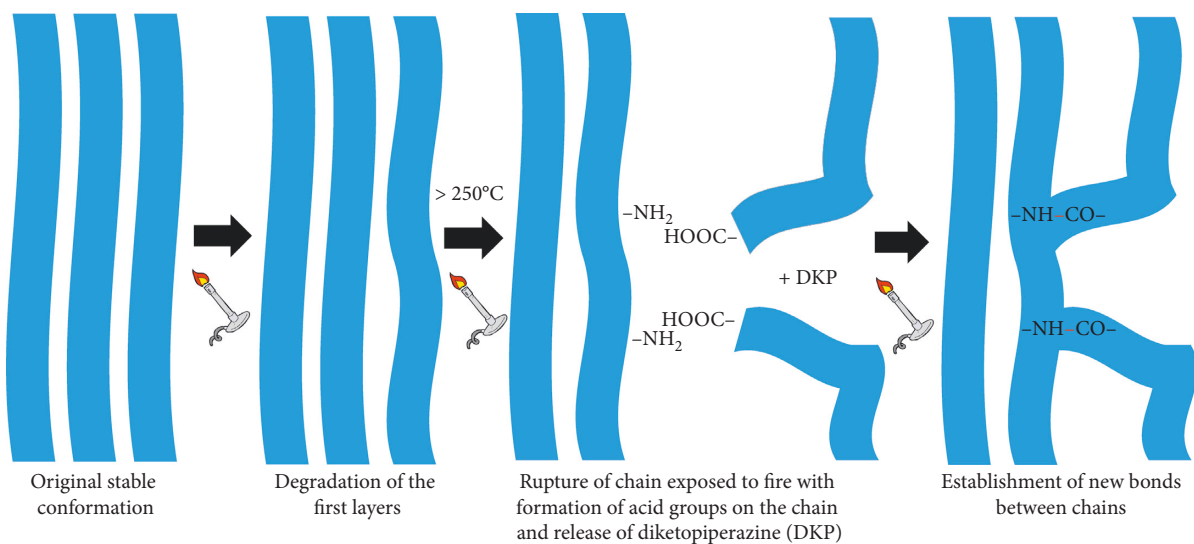


FIGURE 7: Scheme of the possible mechanism for the high resistance of a wet-white leather shavings board against the hot-gun perforation test.

the chemical origin of the plastic-like barrier observed.

- (5) DKP are produced during the degradation process. These gases do not burn [28], and they contribute to the outstanding results observed.

A possible mechanism of proteins rearrangement is shown in Figure 7.

Initially, the proteins have a stable conformation, then, fire/heat goes in contact and the first layers change their arrangement. Longer exposure/higher temperature causes the rupture of the chain by producing DKP and acid-containing moieties. The latter may react with free amino groups of other peptides, building a networked polymer impenetrable for gases. Simultaneously, small molecules such as water, ammonia, NO_x , CO, and CO_2 but also DKPs are produced and they expand inside this networked polymer producing a foam-like structure.

This mechanism could be applied also to mixed wet-white leather shavings wood fibre panels. The acid moieties produced by heating of the leather could also esterify the

hydroxyl groups of wood with the similar result of tightening the structure. In this case, Maillard reactions between carbohydrates and proteins could also be considered [32]; however, the porous-fibrous structure of wood does not allow the establishment of overall impenetrable network, and a minor plastic-like effect was observed; consequently, the results were less performing than the ones observed for pure leather fibreboards.

4. Conclusions

Wet-white leather fibreboards showed outstanding fire resistances. They resisted exposure to the hot-gun perforation test, producing a black smooth overlay coating-like surface impenetrable to gas and a foam-like structure that limits the heat transfer. This barrier could be produced by networking reaction between the acid moieties obtained by degradation process and other amino groups available. During the thermal exposure, diketopiperazine is produced with consequent decreasing of amidic bondings (amide I). The pyrolysis-GC-MS confirms the release of DKP which is not

combustible and hence they can also contribute in limiting the combustion process.

These sustainable biocomposites can be considered for several applications where natural and fire-resistant products are needed. Automotive, nautical, and green building are some of the most interesting sectors where leather-based panels can be suited.

Data Availability

The data were generated during this study.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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