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Tannin-caprolactam and Tannin-PEG formulations as outdoor wood preservatives: weathering properties

Gianluca Tondi¹ · Jinbo Hu^{2,3} · Filippo Rizzo¹ · Janez Buh⁴ · Sergej Medved⁴ · Alexander Petutschnigg¹ · Marie-France Thevenon³

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Abstract

• **Key message** This article presents the leaching, fire and weathering resistance improvements of samples treated with tannin-based wood preservatives added of caprolactam. PEG-added formulations show limited applicability. The FT-IR and ¹³C-NMR analyses of the caprolactam-added formulations show some evidences of copolymerization.

• **Context** Tannin-boron wood preservatives are known for their high resistance against leaching, biological attacks, fire as well as for the good mechanical properties that they impart to wood. These properties promoted these formulations for being a candidate for the protection of green buildings. However, the low elasticity of these polymers and their dark colour implied limited weathering resistances.

• **Aims** The aim of the study is to find suitable additives for tannin-based formulations to overcome their limited weathering resistances, without compromising the other properties.

• **Methods** Treatment, leaching and fire tests, dimensional stability as well as artificial and natural weathering of the timber treated with caprolactam-added and PEG-added formulations were performed. FT-IR and ¹³C-NMR of the formulations were presented.

• **Results** The presence of caprolactam improved the properties of the formulation with particularly significant results in terms of resistance against leaching and dimensional stability. These enhancements were imparted also to the weathering resistance of the tannin-caprolactam formulations. Indeed,

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Jinbo Hu: sample preparation and fire testing

Filippo Rizzo: responsible for the weathering test and the CIELAB system

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the colour changes during the artificial and natural exposures were stable for longer periods. FT-IR and ^{13}C -NMR investigations of the advanced formulations were led, and covalent copolymerization of the caprolactam with the tannin-hexamine polymer was observed.

• **Conclusion** The tannin formulations with caprolactam improved the durability of the wood specimens, while the PEG-tannin presented strong application drawbacks.

Keywords Condensed tannin · Timber protection · CIELAB system · Natural copolymer · Multivariate data analysis · PCA

1 Introduction

In former times, universal solutions for preserving wood were used: Creosote, pentachlorophenol and then chromate-copper-arsenate (CCA) were dominating the market warranting very long service life (Richardson 1993; Ruddick 2011). Since over a decade, bans and restrictions on the use of these wood preservatives have focused attention on technological developments of alternatives in wood protection area (Evans 2003; Schultz et al. 2007; 98/8/EC 1998; 2003/2/EC 2003; 2011/71/EU 2011).

As the wood protection sector is getting under scrutiny, different alternative systems, mainly based on natural solutions, are receiving more attention (Singh and Singh 2012; Mai et al. 2004). Amongst different approaches, the addition of hydrophobic substances in order to hinder the access to water enhancing the durability of wood especially against fungal agents is one of the most suited solutions. Wood protection can be improved by the use of oil and waxes (Treu et al. 2004; Lesar and Humar 2011), as well as tall oil, a secondary product of the pulp and paper industry (Hyvönen et al. 2006), or pyrolysis fractions (Temiz et al. 2010; Palanti et al. 2011; Mazela 2007). Other alternative solutions based on lactic acid and proteins were also studied with promising results (Nöel et al. 2009a,b; Thevenon et al. 1997; Thévenon and Pizzi 2003; Polus-Ratajczak and Mazela 2004). Other researchers have published studies in which the hydrophobic matrix was mixed to an active biocide in order to enhance its protective effect (Evans et al. 2009; Temiz et al. 2008; Yang et al. 2006).

The technology applied in this work exploits the properties of tannins to its utmost as: On one hand, they are easily soluble in water, and therefore, they can penetrate into wood (Tondi et al. 2013a), and on the other hand, they can polymerize in situ increasing the hydrophobicity of the wood surface (Tondi et al. 2012a). Furthermore, tannins are known for their natural biocide activity (Sen et al. 2009) even if their efficacy decreases after polymerization (Thevenon et al. 2009).

The idea of using tannin as wood preservatives has been known for three decades (Laks et al. 1988), and it was successively pursued by several research groups (Yamaguchi and

Okuda 1998; Taylor et al. 2006; Tascioglu et al. 2012) in the following years. A significant breakthrough in the chemistry of flavonoid tannins was that their condensation reactions occurred with similar extent as phenol and resorcinol (Pizzi 1980; Pichelin et al. 1999), and therefore, it was possible to oppose the long-standing leaching problem of tannin in the wood preservation field and hence raise this approach to a new level.

The technology uses the polymerization of tannins and consists in infiltrating the activated oligomers of flavonoid in the wood with a successive in situ polymerization catalysed by heat (Thevenon et al. 2010). This can also be obtained in the presence of an active ingredient such as boric acid. Such associations allow combining the effects of both ingredients, using boric acid at a very low level and observe the restrictions on the use of boron compounds (2008/58/EC 2008), avoid boric acid leaching and increase performances and service life of such treated timber (Obanda et al. 2008).

Original formulations based on tannin-boric acid synergy have shown outstanding preservation properties against biologic attack and fire and have also improved mechanical properties (Tondi et al. 2012b; Tondi et al. 2014). However, the tannin-based treatment does not improve significantly the weathering resistance (Tondi et al. 2012c). The tannin polymer indeed is rigid and dark, and these two conditions carry (i) to mechanical polymer cracking during the continuous dimensional changes occurring when the wood is exposed outdoors and (ii) to higher radical degradation due to light exposure (Tondi et al. 2013b).

The idea of adding other template components to the original formulation considers two different technological approaches: Firstly, an unreactive polyether such as polyethylene glycol (PEG) was added as “steric hindering” filler to decrease the amount of cross-links in the hardened network, and secondly, a polymerizable molecule such as caprolactam, which can polymerize to polyamides producing protein-like polymers, was added to actively participate to the synthesis of a more linear copolymer (Pizzi 1994). Both approaches were considered to enable the polymer to become more elastic and clearer with the objective of producing high-performance wood preservatives. Retentions, resistances against leaching and fire, dimensional stability and colour changes during natural and artificial weathering are described in this paper, and preliminary FT-IR and ^{13}C -NMR investigations on the advanced tannin-based formulations are also presented.

2 Materials and methods

2.1 Materials

Mimosa (*Acacia mearnsii* de Wildt) tannin extract was supplied by Silva Chimica (Cuneo, Italy), while

hexamethylenetetramine (hexamine), boric acid, sodium hydroxide, caprolactam (ϵ -caprolactam) and polyethylene glycol 400 (PEG) were provided by Sigma-Aldrich. The scots pine (*Pinus sylvestris* L.) sapwoods were provided by two different sawmills of Kuchl (Austria).

2.2 Impregnation method

Scots pine samples of various dimensions were cut from stabilized sapwood portions and successively oven-dried at 103 °C until constant weight (Mo). All treatments were performed on anhydrous wood blocks using a single vacuum pressure impregnation: The cycles consisted of 30 min at 8 mbar in a desiccator, the tannin-based wood preservative solution was then introduced and the pressure was slowly increased up to ambient pressure. The specimens were kept under the tannin-based solution for 24 h. After the impregnation treatment, the treated wood samples were removed and blotted with filter paper. The weight of the wet samples was recorded (Mw), and the wet (Rw) and dry (Rd) retentions of active ingredients (tannin, boric acid) were calculated based on the following (Eqs. 1 and 2).

$$Rw = \frac{(Mw - Mo)}{V} \quad (1)$$

$$Rd = \frac{(Md - Mo)}{V} \quad (2)$$

In these equations, Mo is the anhydrous weight before treatment (kg), Mw is the wet weight after treatment (kg), Md is the anhydrous weight after treatment and resin hardening and V is the volume of wood blocks (m³). The retention of the single components was calculated multiplying the wet retention for the concentration by weight of Table 1.

The treated specimens were kept 16 h in the oven at 103 °C to allow the tannin resin to harden (Thevenon et al. 2010). The weight of the dry samples was further registered, and the impregnated wood blocks were then reconditioned at 20 °C and 65% RH until constant mass before testing.

The tannin formulations tested were prepared according to Table 1 and following the method reported by Tondi et al. (2013b), caprolactam and PEG being considered as additives.

2.3 Leaching

Twenty samples for each treatment of dimensions 50 × 25 × 15 mm (L, R, T) underwent two leaching procedures: The first was done according to the directives of the NF X 41-569 (2014) by dipping the treated samples under water with continuous stirring with exchanging the water at 1, 2, 4, 8, 16 and 48 h. The second leaching process was done according to EN 84 (1997), dipping the treated specimens in water and vacuum impregnated, followed with successive water exchange after 2, 26, 50, 74, 98, 122, 146, 170, 194 and 218 h.

The tannin released was quantified with an UV-spectrometer Spectroquant Nov. 60 from Merck measuring the absorbance of the leaching water at the wavelength of 340 nm in which tannin presents a maximum of absorption. The concentration of the solutions was then calculated according to the calibration curve obtained with solutions of known tannin concentration (pH 9.0). Data were successively elaborated so that the sum of the released tannin was reported at each leaching step.

2.4 Fire resistance

Untreated, treated and leached samples of 50 × 25 × 15 mm³ (L, R, T) were exposed to direct short time flame contact tests (Tondi et al. 2014). The samples were exposed to the blue-roaring flame of the Bunsen burner (9-cm distance between the sample and the flame source). Ignition time, flame time and ember time were registered. Each formulation was tested five times, and the data were averaged.

2.5 Dimensional stability

Six treated samples per treatment with dimensions 10 × 20 × 20 mm³ (L, R, T) were dried until anhydrous state and exposed to constantly increasing humidity conditions for 1 week for each step. The radial and tangential dimension measurements were collected at 20 °C with relative humidity of 0, 10, 20, 30, 40, 50, 60, 70, 80, 90 and 95%. Untreated sapwood pine samples were used as controls. The dimensions were taken for every sample and reported as percentage increase before averaging.

Table 1 Percentage by weight of substances used for the preparation of the tannin-based wood preservatives

Formulation	Tannin (%)	Boric acid (%)	Hexamine (%)	NaOH (%)	Additive (%)	Water (%)
Tannin-boron 10%	9.73	0.49	0.58	0.49	–	88.72
Tannin-boron 20%	19.12	0.96	1.15	0.96	–	77.82
Tannin-caprolactam-boron	8.14	0.41	0.49	0.41	15.56	75.01
Tannin-PEG-boron	9.72	0.49	0.58	0.49	19.41	69.34

2.6 Weathering

Series of five samples of treated and untreated scots pine sample of dimensions $70 \times 50 \times 20 \text{ mm}^3$ (L, R, T) were exposed to artificial and natural weathering.

The colour of the surface was monitored with the Mercury 2000 spectrophotometer (Datacolor) after regular intervals of exposure. Six measurements (at defined positions) for each sample were recorded. The diameter of the spotlight used for measurement was 11 mm. The wood colour was determined according to the CIELAB space with CIE standard illuminates D65 and a 10° standard observer.

2.6.1 Artificial QUV

The simulated weathering was carried out in a QUV/spray accelerated weathering tester (Q-Panel Lab Products Cleveland, USA) according to the guidelines of EN 927-6 (2006).

The exposure cycles started with a condensation phase (24 h), followed by short intervals of UV light (2.5 h) with UVA-430 lamps and water spraying (0.5 h). The duration of the artificial weathering test was 1008 h. The evaluation of the colour of the samples was carried out at 0, 168, 336, 504, 672, 840 and 1008 h in six points per sample and averaged.

2.6.2 Natural weathering

The natural weathering tests were done fixing the untreated and the tannin-treated specimens in a 45° grid located in Kuchl (Austria) and exposed to south for 2016 h of weathering (between 16 September 2013 and 9 December 2013). The evaluation of the colour of the samples was carried out at 0, 168, 504, 672, 1008, 1512 and 2016 h in six points per sample and averaged.

2.7 FT-IR analysis

Polymers of tannin-hexamine and the components of the advanced formulations were prepared as follows: Thirty grams of tannin-hexamine solution 30% at pH 9.0 was prepared and divided into three test tubes: one reference and two tubes were added 6 g of solid caprolactam and PEG, respectively. The three test tubes were manually mixed until homogeneous and sealed before being exposed to 103°C for 24 h. The three formulations presented viscous liquid/solid, and therefore, a few milligrams of each test tube was removed and dried in a petri dish at 60°C for 4 h. The three solids, the PEG and the caprolactam were scanned three times in a PerkinElmer Frontier FT-IR spectrometer between 4000 and 650 cm^{-1} , with a resolution of 4 cm^{-1} and 32 scans. The obtained spectra were averaged, baseline corrected and normalized with Unscrambler X version 10.3 software by Camo (Oslo,

Norway). The principal component analysis was carried out using the NIPALS algorithm.

2.8 ^{13}C -NMR analysis

The polymers of tannin-hexamine and tannin-hexamine caprolactam prepared in the same way as previously described for the FT-IR analysis were measured at 25°C with an Ascend 500 NMR spectrometer by Bruker (Germany). The instrument settings were optimized for carbon (^{13}C) detection, and the measurements were performed with 62.90 MHz for 1000 transients and relaxation time of 5 s.

3 Results

3.1 Retentions

The wood preservative uptake is possibly one of the most important parameters to be investigated when a wood preservative is tested. It was observed that the scots pine samples were generally easily impregnable with low tannin content formulations (Fig. 1a, b).

Significantly lower liquid uptakes were registered for the samples $70 \times 50 \times 20 \text{ mm}^3$ when 20% tannin solutions were applied. The effect of the sample dimensions is observed also for the 10% tannin solution but to a much lower extent. The presence of caprolactam does not significantly modify the liquid uptake, but the formulations containing PEG showed a generally lower penetrability due to the increase of viscosity of these formulations.

Conversely, the solid uptake was considerably lower for the samples treated with 10% tannin solution and no further additives. The presence of caprolactam and PEG enhances the amount of solid ingredients in wood to the level achieved with the 20% tannin formulation.

These observations suggest that the presence of additives allows a similar penetration of the wooden pieces to the 10% tannin formulation and simultaneously enhances the amount of solid preservative in the structure to the level achieved with 20% tannin preservatives.

Indeed, the samples treated with PEG register high standard deviations because the surface presents an observable viscous layer which becomes much thicker as soon as the samples are kept under water for a while. This PEG gelatinous skin is probably due to the accumulation of unpenetrated PEG, and therefore, also the analysis of the results has to take into account this behaviour. According to the mean values, it is possible to calculate the tannin and the boron content in kg/m^3 of wood (Table 2).

These data are affected by very high standard deviations because they come from samples of different dimensions and because the end-grain surfaces were different. However, much

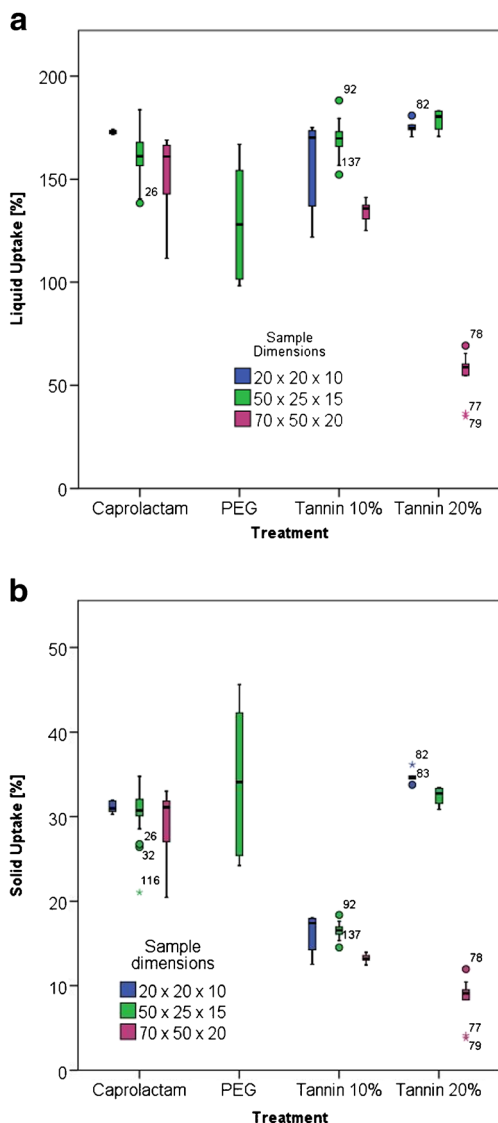


Fig. 1 Retention of the tannin-based formulations against different sample dimensions during the impregnation process: **a** liquid uptake and **b** solid uptake

higher variances are registered for the samples treated with tannin 20% and PEG-modified formulations.

It can be seen that the advanced formulations have a lower tannin and boron content. Hence, it is expected that such treated wood would have a lower biological resistance, unless

boron is very efficiently maintained into the wood (during leaching).

The study of the biological properties of these advanced formulations is discussed in the second part of this work (Hu et al. 2016).

3.2 Leaching behaviour

The resistance to leaching of the advanced formulations was investigated and compared to that of standard formulations (10 and 20% tannin without additives).

In Fig. 2a, b, the amount of leached tannin according to the NF X 41-569 and EN 84 are reported. The results obtained for the 10 and 20% tannin-treated timber confirm the previous tests where only a restrained amount of tannin was leached out (Tondi et al. 2012b). The samples treated with the two advanced formulations, with PEG and caprolactam, show even lower decrease of leached tannin. The tannin loss is always lower than 20% of the original tannin content in the sample when applying the NF X 41-569 procedure. This tendency is confirmed also when using the notoriously drastic EN 84 procedure, for which one the tannin is leached out for less than 15% related to its original amount.

Furthermore, it can also be observed that the amount of tannin leached is similar comparing the two leaching treatment after specific time. This means that both leaching methods are able to leach out a similar amount of tannin suggesting that only the non-reacted tannin oligomers can easily leach out, while the cross-linked fractions stay in wood also when forceful leaching process occurs.

The loss of tannin during leaching is limited for PEG-treated samples. This phenomenon is mostly due to the protective effect of PEG layer which is found all over the wood surface. The appearance of the specimens at the end of the leaching presents a thick gelatinous film of swelled PEG that made the samples unable to be handled. Due to this drawback, the PEG formulation was not further investigated.

The caprolactam-added formulations also showed outstanding leaching resistance. The leaching of tannin for the sample treated with this formulation is around 40% less than that shown by the samples treated with the 10% tannin standard formulation.

Table 2 Retention of tannin and boron in the different tannin-based formulations

Formulation	Wet retention (kg/m ³) (SD)	Dry retention (kg/m ³) (SD)	Tannin content (kg/m ³)	Boron content (kg/m ³)
Tannin-boron 10%	630.5 (74.1)	62.2 (7.4)	61.3	0.53
Tannin-boron 20%	412.3 (238.5)	75.5 (52.4)	78.8	0.69
Caprolactam-tannin-boron	644.5 (42.7)	122.3 (9.1)	52.5	0.46
PEG-tannin-boron	517.0 (109.3)	136.7 (34.7)	50.2	0.44

SD standard deviation

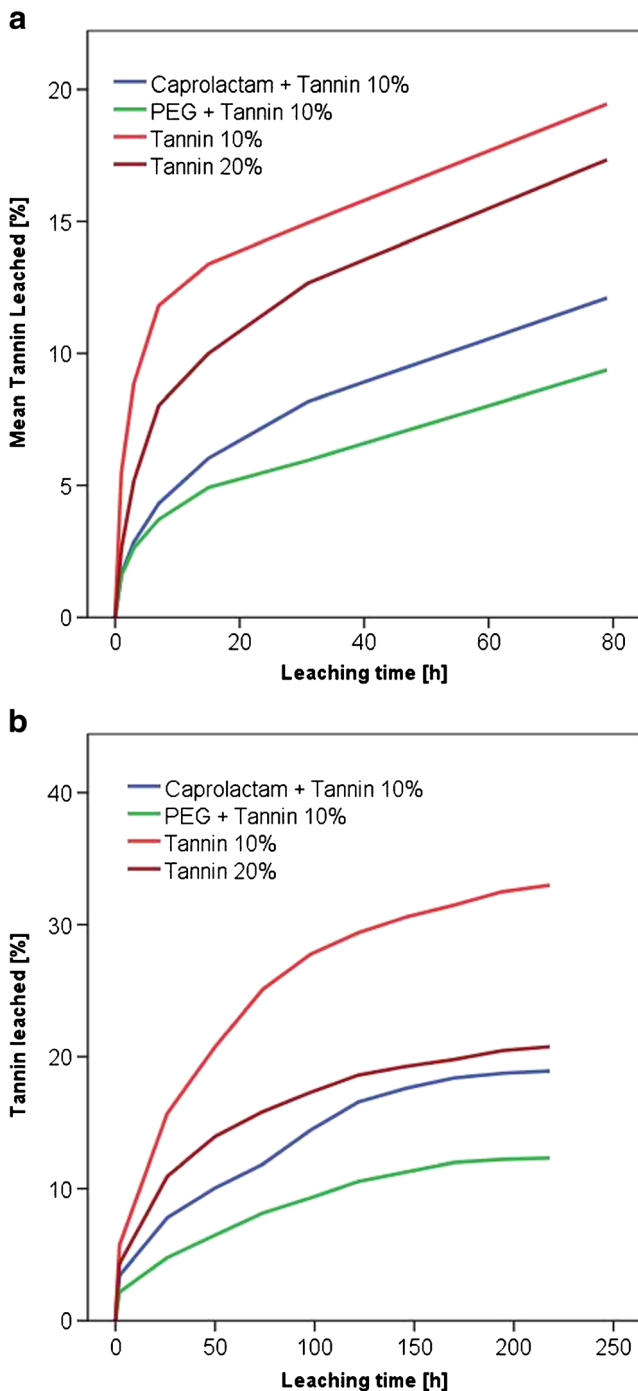


Fig. 2 Percentage of total tannin released during the leaching process: **a** NF X 41-569 and **b** EN 84

In particular, in the latest leaching days of the EN 84 procedure, the amount of tannin leached out is very low, and it represents a threshold for the maximum leaching of tannin, suggesting that no further loss will occur. In addition, the fact that the samples treated with caprolactam show a more homogeneous colour distribution on the surface in comparison with the standard tannin formulation allows to consider that this

advanced formulation is more suitable for active ingredient retentions and thus for outdoor exposures.

3.3 Fire resistance

The fire behaviour of the formulation treated with caprolactam is compared with the values of the standard formulations, and results are reported in Table 3.

It looks evident that the addition of caprolactam decreases the fire resistance of the tannin-boron standard formulation even if a mild improvement is still observed when the formulation is compared to untreated scots pine.

3.4 Dimensional stability

The dimensional stability of the treated samples is another important parameter for evaluating the stresses occurring in wood during weathering. One of the main hypothesis made for explaining the low weathering resistance of the standard tannin formulation was their highly rigid behaviour that led to polymer cracks during dimensional changes induced by weathering.

In Fig. 3, the radial and tangential dimensional changes are depicted.

The two figures show that the presence of caprolactam in the formulation decreases the affinity of the wood specimens for water, and therefore, lower swellings in radial and tangential direction are observed. A certain contribution to this tendency is that the amount of the “hydrophilic” tannin uptake is slightly decreased. However, it cannot be excluded that the higher amount of solid preservative up-taken creates a more resistant polymer by increasing the tensions inside these samples. Hence, it is expected that during outdoor exposures, the

Table 3 Ignition, flame and ember time of caprolactam tannin-treated wood in comparison with the “standard” formulations

Formulation	Ignition time (s)	Flame time (s)	Ember time (min)
Untreated	8.6	192	4.9
Tannin-boron 10%	75 ¹	35 ¹	2.5 ^a
Tannin-boron 20%	110 ²	15 ²	0.9 ^b
Caprolactam-tannin-boron	12.7	185	3.9
Caprolactam-tannin-boron (leached NF X 41-569)	12.5	180	4.1
Caprolactam-tannin-boron (leached EN 84)	12.8	178	4.1

^a Tondi et al. (2012a)

^b Tondi et al. (2013b)

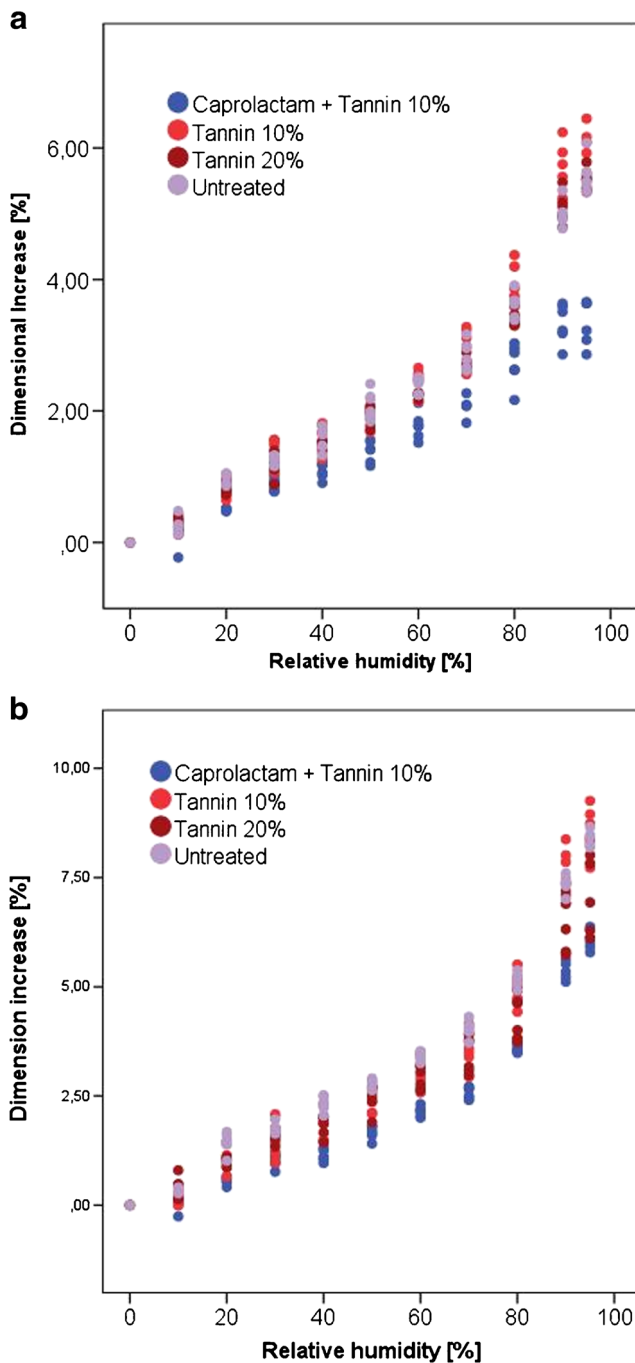


Fig. 3 Dimensional swelling of untreated, 10 and 20% tannin-treated scots pine specimens compared with tannin-caprolactam-treated samples under different RH conditions at 20 °C. **a** Radial swelling and **b** tangential swelling

caprolactam-tannin-treated samples will better prevent the swelling/shrinkage strain producing a more stable material in which reduced amount and intensity of cracks will be observed (Hansmann et al. 2006). The better distribution of the wood preservative in the material suggests also that its properties will resist unchanged also in a long run weathering exposure.

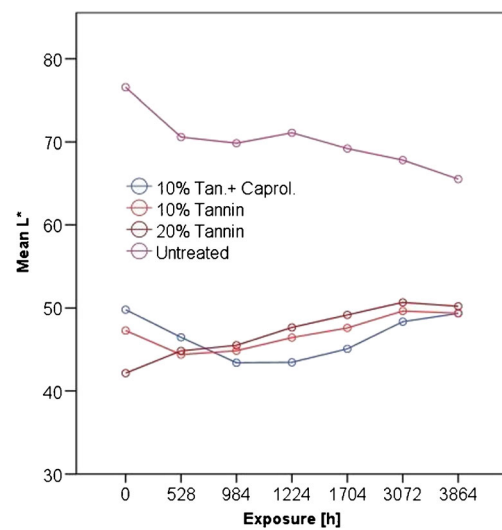


Fig. 4 Trend of the colour coordinate lightness (L^*) during artificial weathering test

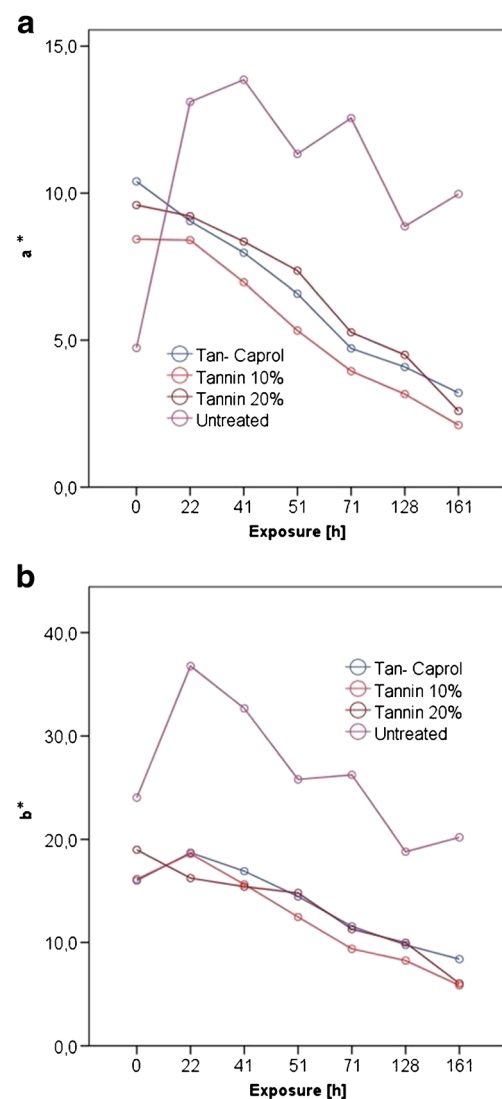


Fig. 5 Trend of the colour coordinate a^* and b^* during artificial weathering test

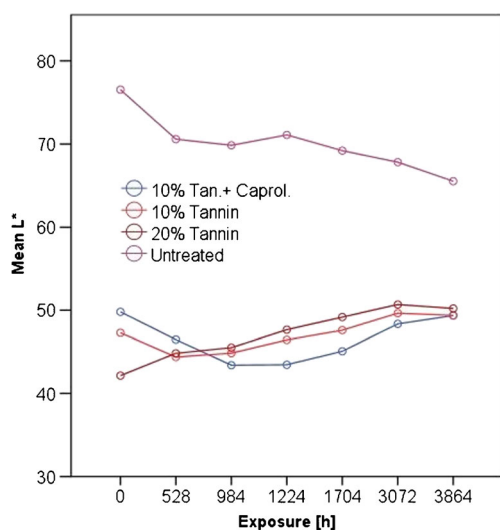


Fig. 6 Trend of the colour coordinate L^* during natural weathering test

3.5 Weathering

Notwithstanding the considerable advantage carried by the addition of caprolactam, the key tests for the evaluation of these wood preservatives are undoubtedly the weathering tests.

The artificial weathering tests were followed monitoring the colour of the surface after different time lapses. According to our previous work, L^* is the more appropriate parameter to describe the effects of weathering (Tondi et al. 2013b). The evolution of this parameter during weathering is given in Fig. 4.

It can be observed that at the beginning of the experiment, the caprolactam-modified samples have a slightly lighter colour than the other tannin-treated specimens. After 168-h exposure, the colour turns darker and becomes very similar to that of the standard formulations. Then, the greying begins, and it can be observed that the caprolactam-modified samples converge also to the grey level of untreated wood but significantly more slowly than the samples treated with the standard formulations.

These observations suggest that the polymer of tannin containing caprolactam resists the weathering better than the standard formulation even if it still have the tendency to reach the grey level of the untreated specimens.

The a^* and the b^* values, the yellow-blue and the green-red components of the colour, respectively, do not significantly change between the advanced tannin formulations and the standard ones (Fig. 5a, b).

In particular, the component a^* shows a continuous fading of the red turning to greenish, and the b^* component gets also a negative slope underlining that the colour tends to turn blue. The general aspect of the surface tends to grey; however, the caprolactam-modified formulations maintain a lower value of L^* for longer time, meaning that the tannins remain longer in the wood samples.

The natural weathering shows the same trend (Fig. 6) confirming the retention of the tannin polymer into the wood samples.

It has to be noticed that the trend observed for the weathering test is repeated also in the natural weathering, with the only difference of showing a degradation of the advanced

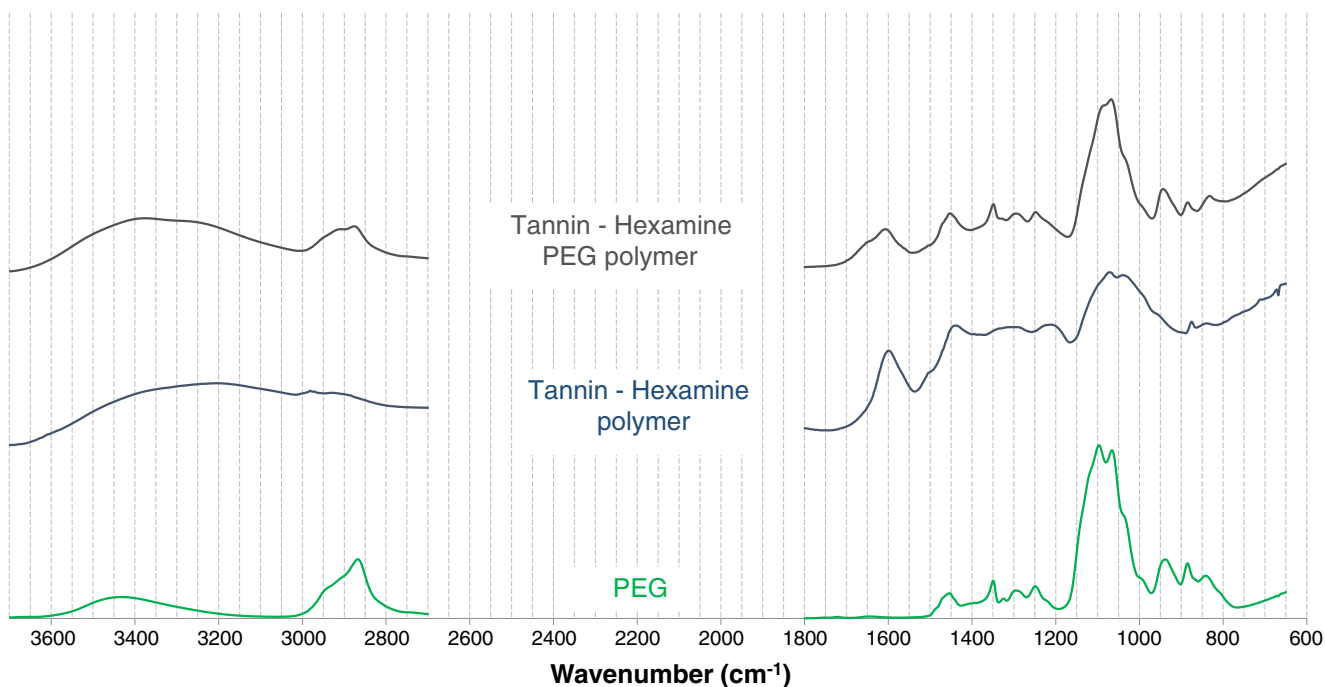


Fig. 7 FT-IR spectra of the tannin-hexamine-PEG blend compared with the tannin-hexamine polymer and the PEG

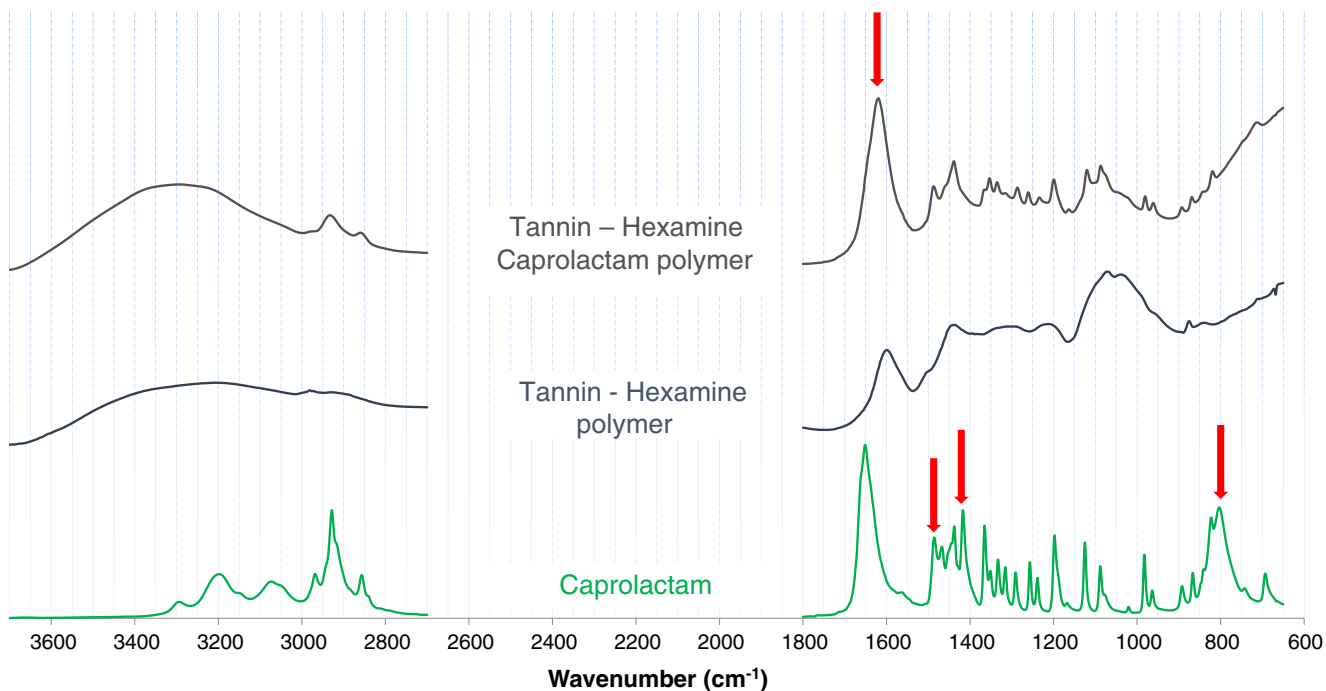


Fig. 8 FT-IR spectra of the tannin-hexamine-caprolactam blend compared with the tannin-hexamine polymer and the caprolactam

formulation very similar to the standard formulations. This decrease of lightness occurs in the final part of the exposure which coincides with the period after several days of snow.

The cold temperatures of the period of exposure suggest internal stress of the wood much higher than during the dimensional stability test because the daily cycle of ice formation/melting undergoes the wood to higher solicitations, able to break down also the tannin-caprolactam copolymers.

3.6 FT-IR and ^{13}C -NMR analysis

In the following Figs. 7 and 8, the FT-IR spectra of the two advanced formulations are reported and compared with the standard tannin-hexamine polymer (Schnabel et al. 2014) and the pure additives.

It can be observed in both figures that almost all the vibrational signals of the advanced formulations are obtainable by

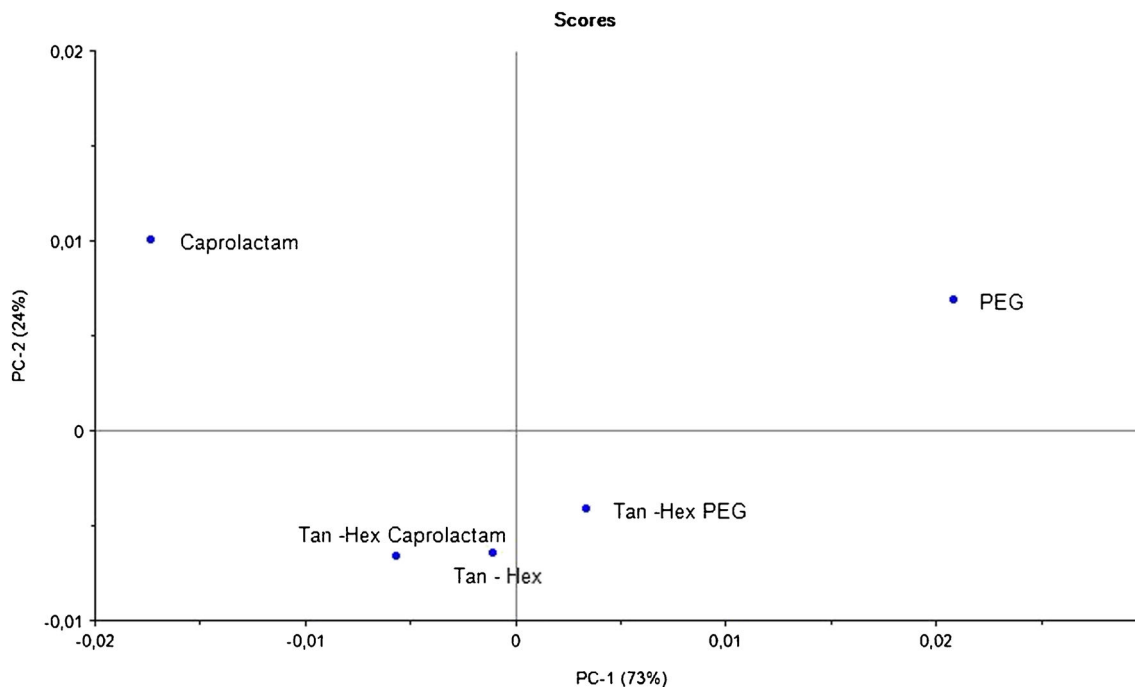


Fig. 9 Principal component analysis of the five spectra

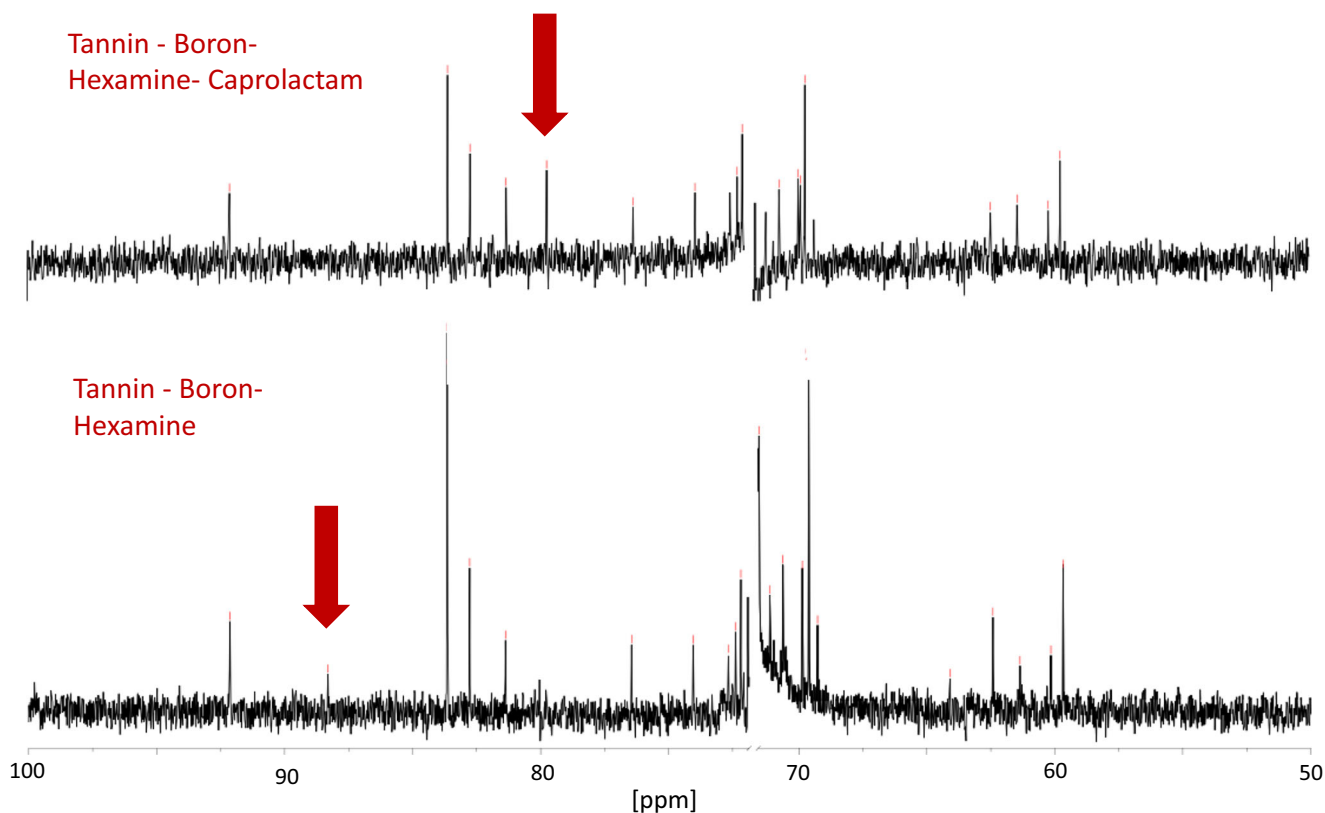


Fig. 10 C-NMR of tannin-boron-hexamine and tannin-boron-hexamine-caprolactam polymers

superposition of the tannin-hexamine polymer and the pure additive. In the case of PEG, no new signal is observable or disappearing. It seems that no copolymerization between PEG and tannin-hexamine occurs. Conversely, in the formulation containing caprolactam, there are a few differences that have to be noticed. The signal of C=O stretching of amide is shifted from 1650 to 1620 cm^{-1} , while the signals at 1560 , 1415 and 820 cm^{-1} are not observed in the polymer (see arrows). However, the attribution of the signals is not easy, and therefore, the principal component analysis was done in order to extrapolate the maximum of the information. In Fig. 9, the two principal components (PC1 and PC2) are represented in a Cartesian graphic.

The main principal component (PC1 = 73%) classifies the chemical aspect of the formulations in three main classes: (i) the amides, (ii) the polyether and (iii) the flavonoids. The two advanced formulations are correctly located between the tannin-hexamine polymer and the respective pure additive. The second principal component (PC2 = 24%) distinguishes between the tannin polymer and the pure bases, and it considers the formulation tannin-hexamine caprolactam very similar to the one of tannin-hexamine, while the tannin-hexamine-PEG also in this case shows intermediate values between the tannin-hexamine and the pure PEG. Further investigation with ^{13}C -NMR was required for a better understanding of the

chemistry of tannin-hexamine-caprolactam, and the spectra of the tannin-hexamine and tannin-hexamine-caprolactam are presented in Fig. 10.

It can be observed that in the region around 79.38 ppm , a new signal occurs. This signal was not present in the spectra of caprolactam, and therefore, it belongs to a carbon with new surroundings. This signal belongs to a new species $\text{R}-\text{CH}_2-\text{O}-$, and hence, a new ether bond occurs. This evidence confirms that a new covalent copolymer is formed between caprolactam and the tannin-hexamine. It has to be noticed that a small signal at 88.31 disappears when caprolactam is added. This signal can be attributed to carbons between two electro-negative atoms, and in particular, a $-\text{O}-\text{CH}_2-\text{O}-$ moiety would be the more probable. This could be attributed to the presence of traces of consecutive methylene ether bridges.

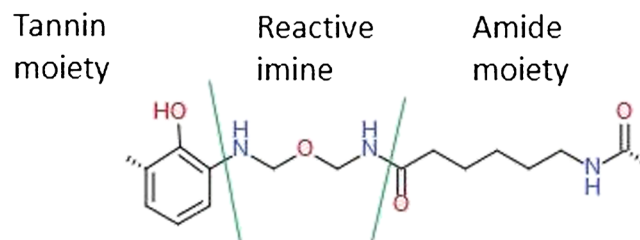


Fig. 11 Possible polymer structure of a tannin-hexamine-caprolactam polymer

4 Discussion

The advanced tannin-boron formulations have presented opposite behaviour. The formulation in which PEG was added presented average wet retentions and high solid uptake with very high standard deviations. This meant that the formulation was not able to penetrate into the wood and that most of the solid was accumulated on the surface. This drawback became very important when the samples were immersed in water. The unpenetrated PEG took up water and formed a transparent gelatinous layer of a few millimetres.

The FT-IR confirmed that there was no chemical linkage between the PEG and the tannin-hexamine polymer.

Completely different results were observed for the caprolactam-added formulations. High wet and dry retentions as well as contained standard deviation suggested a very good penetration of the wood preservative and a homogeneous distribution of the latter. The positive leaching resistance and the improved dimensional stability suggested that the caprolactam intimately connect with the tannin polymer and that it participated in rendering the surface less penetrable by water even when the leaching process applied was very intense (EN 84). These improvements were reflected also in the weathering which presented a considerable enhancement of the outdoor durability of these formulations. As expected, the addition of an organic substance decreased the performances against fire of the formulation.

The FT-IR analysis of the caprolactam formulations presented some modifications which mostly consisted in signal loss. This can be interpreted like a polymer formation with the overlapping of many bands. The PC analysis showed a very similar value of PC2 with the original tannin-hexamine which might imply a certain degree of inclusion in the polymer. The ^{13}C -NMR investigation confirmed that new covalent bondings are occurring when caprolactam is added to the tannin-hexamine formulation.

According to the literature, caprolactam in water evolves rapidly to aminocaproic acid, and in alkaline environment, the process of polymerization can occur as well especially if catalysed by temperature (Ritz et al. 2005). The inclusion of the monomeric aminocaproic acid or its oligomers in the tannin-hexamine network can be figured out in many ways. According to the signal of $\text{R}-\text{CH}_2-\text{O}$, the more probable hypothesis is that the reactive imines produced from hexamine in alkaline environment react with the carboxylic group of the caprolactam (Pichelin et al. 1999). Here, a possible polymer structure is observed (Fig. 11).

The phenolic part on the left side represents the tannin; the amino ether shows the interconnection due to the reactive imines, and the amide from the aminocaproic acid shows the continuation of the polymer.

5 Conclusions

The use of PEG and caprolactam to increase the weathering resistance of the tannin polymer has led to interesting results. It was observed that even if the impregnation treatment was possible for both the additives, the PEG-added formulation developed a gelatinous surface layer when dipped in water. This feature has excluded the use of PEG-tannin formulation for outdoor applications. Conversely, the advanced tannin-caprolactam formulation gave positive results that can be summarized in improved leaching resistance, improved dimensional stability and improved weathering resistance compared to the standard tannin-boron formulations. These formulations presented also very satisfactory retentions and enhanced fire properties compared with untreated wood. The FT-IR investigations of the two advanced formulations have confirmed that the PEG does not covalently bind with the tannin polymer, while some evidence of polymerization are observed for the caprolactam-added formulations which were confirmed by ^{13}C -NMR. The interesting results obtained including caprolactam in the tannin-hexamine copolymer offer the opportunity to produce environmentally friendly, high-performing solutions in which other natural polyamides like proteins can be suited for the protection of wood.

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Compliance with ethical standards

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