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# Self-Healing UV-Curable Acrylate Coatings for Wood Finishing System, Part 2: Impact of Monomer Structure and Self-Healing Parameters on Self-Healing Efficiency

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Abstract: Wood is increasingly used in construction for the benefits it brings to occupants and for its ecological aspect. Indoor wood products are frequently subject to mechanical aggressions, their abrasion and scratch resistance thus need to be improved. The coating system ensures the wood surface protection, which is, for wood flooring, a multilayer acrylate UV-curable 100% solid system. To increase the service life of wood flooring, a new property is studied: self-healing. The objective of this study is to observe the impact of monomer structure on self-healing efficiency and the effect of self-healing parameters. A previous formulation was developed using hydrogen bond technology to generate the self-healing property. In this paper, the assessment of the formulation and the self-healing parameters' impact on self-healing efficiency as well as the physicochemical properties are presented. The composition of the monomer part in the formulations was varied, and the effect on the conversion yield (measured by FT-IR), on the Tg and crosslinking density (measured by DMA) and on mechanical resistance (evaluated via hardness pendulum, indentation, and reverse impact) was analyzed. The self-healing efficiency of the coatings was determined by gloss and scratch depth measurements (under constant and progressive load). It was proven that monomers with three acrylate functions bring too much crosslinking, which inhibits the chain mobility necessary to observe self-healing. The presence of the AHPMA monomer in the formulation permits considerably increasing the crosslinking density (CLD) while keeping good self-healing efficiency. It was also observed that the self-healing behavior of the coatings is different according to the damage caused. Indeed, the self-healing results after abrasion and after scratch (under constant or progressive load) are different. In conclusion, it is possible to increase CLD while keeping self-healing behavior until a certain limit and with a linear monomer structure to avoid steric hindrance. Moreover, the selection of the best coatings (the one with the highest self-healing) depends on the damage.

Keywords: acrylate; UV curable; self-healing; hydrogen bonds; crosslinking

# 1. Introduction

Wood is a natural material with a lot of benefits. It has been proven that being in contact with the natural elements reduces stress, maintains the feeling of well-being, and increases productivity and performance. This phenomenon, called biophilia [1], was elaborated by the biologist Edward O. Wilson in 1986 [2]. Many institutions consider the biophilia in construction projects [3] by increasing the use of wood as indoor material in walls, floors, or furniture. Moreover, wood is an ecological material as it stores the carbon dioxide captured by the tree during its life. Using one cubic meter of wood in



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**Copyright:** © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). construction allows for the storage of one ton of atmospheric  $CO_2$  [4]. As wood use increases in construction, it is important to ensure wood resistance to mechanical and chemical aggressions. This also permits the improvement of wood service life.

The surface mechanical resistance of wood planks is ensured by increasing wood hardness via mechanical [5] or chemical [6] ways. Surface protection again chemicals is provided by coating deposition on the wood plank. Scratches are the most frequent damage to wood furniture. Therefore, scientists have worked to improve the scratch resistance of wood coatings for the last 10 years. Another way to avoid scratches is to repair them thanks to a self-healing coating. Self-healing is a new property developed by material scientists to increase the service life of materials [7], but in the wood sector, it is not yet frequently used. For prefinished wood flooring, UV-curable 100% solid acrylate coatings are the most often used, as they are highly crosslinked and polymerize quickly. The fast polymerization guarantees high production speed, and the absence of solvents avoids VOC emissions [8]. Wood flooring UV-curable coating systems are composed of several layers: one primer, several sealers, and one topcoat. The white scratches are the ones that cut the coating. As the topcoat of this type of system is very thin, it has been decided to work on the sealer layers that represent most of the coating. Thus, to develop a self-healing wood flooring coating system, it is necessary to formulate a new UV-curable 100% solids acrylate sealer.

Several technologies were developed to prepare a self-healing material, the extrinsic ones (vascular and capsule-based) and the intrinsic ones [7]. The vascular technology uses capillaries filled with a self-healing agent. The damage breaks the capillaries, and the healing agent flows into the scratch and fills it. To create these capillaries inside the material, direct ink writing is used [7]. Unfortunately, this is not usable during inline processes for the wood coating industry.

The capsule-based technology is widely used for bulk materials such as cement and concrete [7]. The healing behavior is similar to vascular technology: The scratch breaks the capsules, which release its healing agent inside the scratch. At the opposite of capillaries, the capsules are dispersed in the coating formulation before application. Therefore, this technology does not impact the application procedure and is applicable to the wood coating industry. The self-healing behavior is autonomous with the capsule-based technology, neither heat nor external stimuli are necessary. However, the capsules can be used only once, so the healing is not repeatable in the same area [7].

Intrinsic technologies are based on reversible bonds in the coating [7]. These bonds are broken by the kinetic energy of the damage, then the rebounding under stimuli ensures the self-healing. This technology permits repeatable healing but is not always autonomous. It applies to a large range of materials as it does not impact the application procedure [7].

Indoor wood products are subject to repeatable damage. Thus, a repeatable healing strategy is well suited for wood flooring. Consequently, the intrinsic self-healing technology was selected to develop a self-healing wood flooring coating.

Many materials with intrinsic self-healing properties have been developed but for soft materials such as flexible oligomers or hydrogels. The reversible bonds used are the reversible covalent bonds, weak bonds, and molecular tangles [7]. They break and rebound under external stimuli, creating a dynamic network [7,9,10]. Molecular tangles are interactions needing only chain mobility, meaning that the self-healing materials based on this interaction do not require external stimuli. As the interaction is spontaneous, it is only necessary to put the edges of the damage in contact to observe the self-healing. This technology concerns materials with high chain mobility at room temperature, such as silicones or hydrogels [7]. The UV-curable wood flooring must be highly crosslinked to ensure good mechanical resistance. As a result, there is no chain mobility within these coatings at room temperature, so the molecular tangles interaction is not an appropriate choice to develop an intrinsic self-healing UV coating.

Another technology reported in the literature is the covalent bond involved in reversible reactions, such as the Diels–Alder reaction [11–13]. A self-healing polymer using Diels–Alder reactions was developed by Chen et al. [11]. Their polymer was composed

of furan and maleimide to ensure crosslinking. However, the retro Diels–Alder reaction occurs at high temperatures, and the yellowing of furan is observed after heating. All the materials using this technology must be heated over 100 °C to observe self-healing. This is due to the retro Diels–Alder reaction, which involves breaking a covalent bond (200–400 kJ/mol), so the temperature necessary is between 100 and 150 °C [7,10,11]. This temperature is an important drawback for wood products as it may cause overdrying above 100 °C.

The last reversible bonds are the weak bonds: van der Waals,  $\pi$ interactions, and hydrogen bonds. These three have lower bond strength than covalent bonds, so the heating to ensure self-healing is kept below 100 °C, making the weak bonds usable to develop self-healing UV-curable coatings for wood flooring. The other important point to consider is the hardness, which is necessary for wood flooring coatings to resist daily aggressions. The stronger the bonds in the material are, the harder the polymer will be [14]. In this regard, hydrogen bonds were chosen to develop an intrinsic self-healing UVcurable coating for wood flooring, as it is the strongest weak bond [15]. Several polymers presenting self-healing behavior thanks to hydrogen bonds are present in the literature. As an example, Chen et al. [16] reported a multiphase elastomer where the hydrogen bonds of the polyamide phase ensure self-healing. Studying the impact of the hydrogen bond quantity on the self-healing, Liu et al. [17] noticed that increasing the concentration of hydrogen bonds requires a higher temperature to observe the self-healing. In addition, Cortese et al. [18] proved that adding hydrogen bonds increases the crystallinity of the polymer, which inhibits chain mobility. This means that there is an optimum quantity of hydrogen bonds to obtain a polymer that has enough hydrogen bonds to ensure selfhealing and provide mechanical resistance but not too much to avoid the chain mobility inhibition and a thermal stimulus at too-high temperatures.

Most of the literature on UV-curable self-healing polymers concerns polyurethanes. For instance, Wang et al. [19] published a study on self-healing UV-curable polyurethane acrylate based on the Diels–Alder reaction. UV-curable polymers using hydrogen bonds to ensure self-healing are mostly applied on lightly crosslinked materials, such as in the study of Liu et al. [17], who developed a polyurethane oligomer with self-healing properties via hydrogen bonds. This also applies to acrylate polymers. Fan et al. [20] studied the mechanism of an industrial acrylic elastomer, reported one example of self-healing acrylate material. They indicate that the self-healing behavior was based on molecular tangles. Few articles only present self-healing on cross-linked acrylate polymers. One of them is from Abdallh et al. [21], which synthetized a polyacrylate containing 7-methacryloyoxycoumarin crosslinking and open under UV light stimulus. Nowadays, few self-healing UV-curable acrylate polymers are reported. In our previous paper, we developed a self-healing coating composed by HEMA monomers and Ebecryl 4738 oligomers for wood flooring applications [15].

Our previous study brought to the formulation of a self-healing sealer for wood coatings containing one monomer and one oligomer [15]. The objective of the present work was to evaluate the impact of adding a second monomer in this formulation on the mechanical properties and the self-healing behavior was evaluated. The challenge of the present study is to obtain the optimum quantity of hydrogen bonds to reach high self-healing efficiency without chain mobility inhibition. The hydrogen bond quantity is also crucial to keep the thermal stimulus below 100 °C to avoid wood overdrying. Finally, it is important to improve the mechanical properties of the HEMA–Ebecryl 4738 coating previously developed. This paper presents the formulation of intrinsic UV-curable 100% solid acrylate coatings via hydrogen bonds optimized for wood flooring use. The impact of the composition and the cross-linking on the self-healing efficiency, and the study of self-healing parameters are presented. Formulations with three acrylate components are presented to formulate a resistant and self-healing coating for the wood flooring.

## 2. Materials and Methods

## 2.1. Materials

Chemicals were selected based on the results obtained in our previous study [15]. UV-curable acrylate monomers and oligomers of low toxicity bearing alcohol groups were chosen and are presented in Table 1.

Name	Description	Molecular Weight (g/mol)	Viscosity (cP)	Supplier	Function
AHPMA	3-(Acryloyloxy)-2- hydroxypropyl methacrylate	214.2	44	Sigma-Aldrich	Monomer
PETA	Pentaerythritol triacrylate	298.3	1000	Sigma-Aldrich	Monomer
HEMA	2-Hydroxyethyl methacrylate	130.1	6	Sigma-Aldrich	Monomer
Ebecryl 4738	Aliphatic urethane acrylate, hard resin	confidential	35,000	Allnex	Acrylated allophanate oligomer
HMPP	2-Hydroxy-2- methylpropiophenone	164.2	0	Canlak	Photoinitiator absorbing at 240 nm

**Table 1.** Materials used in coatings formulation.

The reference coating, i.e., the one leading to the highest self-healing efficiency in our previous study, is composed of HEMA and Ebecryl 4738. AHPMA and PETA monomers (Figure 1) were selected to develop formulations with three components and improve the overall performance of the coatings. These monomers have been chosen because they gave high results of hardness pendulum in the previous study [15], which indicates high stiffness. Thus, they can bring rigidity to the developed coatings.



Figure 1. Structure of the acrylate monomers used in the formulations.

#### 2.2. Coating Formulation and Application Procedure

Formulations prepared contain two acrylate monomers, one oligomer, and a photoinitiator. From the most to the least viscous one, chemicals were added in a metallic flask and mixed at 600 rpm for about 5 min using the dissolver DISPERMAT LC30 (VMA, Reichshof, Germany). These formulations are the sealer of a multi-layer coating and must have a viscosity between 2000 and 2500 cP at 10 rpm, applicable with a roller coater at room temperature. The quantity of monomers and oligomers was calculated to reach the targeted viscosity; all the values are presented in Table 2. Viscosities were measured using a Cambridge viscometer VISCOlab 4000 (PAC, Medford, OR, USA). Measurements were taken after stabilization of the viscosity values.

In this study, the impact of adding a second monomer in the self-healing formulation on the mechanical properties and the self-healing behavior was evaluate. Therefore, PETA and AHPMA monomers were added in different quantities to the HEMA–Ebecryl 4738 formulation.

n°	Monomer	Oligomer	m <sub>oligomer</sub> (g)	m <sub>HEMA</sub> (g)	m <sub>2nd monomer</sub> (g)	m <sub>photoinitiator</sub> (g)	η (cP)
1	HEMA		82.5	17.5	х	3	2336
2	90% HEMA 10% PETA		83.2	15.1	1.7	3.2	2285
3	70% HEMA 30% PETA		80.8	13.4	5.8	3	2407
4	50% HEMA 50% PETA	Ebecryl 4738	77.4	11.3	11.3	3.2	2271
5	90% HEMA 10% AHPMA		84.2	14.2	1.6	2.9	2301
6	70% HEMA 30% AHPMA		83.0	11.9	5.1	3.1	2174
7	50% HEMA 50% AHPMA		81.0	9.5	9.5	3.2	2350

Table 2. Viscosity results  $(\eta)$  of one and two hydroxyl component formulations.

Formulations were applied on metallic Q-panels R36 (Q-lab, Westlake, OH, USA) (or glass panel for the pendulum damping test) with a 100  $\mu$ m gap square applicator film PA-5353 (BYK Additives & Instruments, Columbia, SC, USA). Film polymerization was performed using a UV oven ATG 160 305 (Ayotte techno-gaz, Lourdes-de-Joliette, QC, Canada), with a medium pressure mercury light UV mac 10 (Nordson, Westlake, OH, USA) emitting between 200 and 500 nm. The oven was set to obtain a UV irradiation of 150 mW/cm<sup>2</sup> and 200 mJ/cm<sup>2</sup>.

## 2.3. Physicochemical and Mechanical Characterization

#### 2.3.1. Fourier Transformation Infrared Spectroscopy Measurements (FTIR)

Fourier transformation infrared spectroscopy (FT-IR) measurements were employed to determine the conversion yield of the coatings. The Spectrum 400 spectrophotometer (Perkin Elmer, Woodbridge, ON, Canada) was used with an attenuated total reflectance accessory (ATR). Measurements were realized on each film (polymerized) and formulation (liquid) between 650 cm<sup>-1</sup> and 4000 cm<sup>-1</sup> (32 scans by measures, resolution of 4 cm<sup>-1</sup>).

Baseline correction and normalization on carbonyl peak ( $1710 \text{ cm}^{-1}$ ) were applied on each film. Stretching vibration of the carbonyl at  $1710 \text{ cm}^{-1}$  (reference peak) and the twisting vibration of alkene at  $810 \text{ cm}^{-1}$  (Figure 2) were used to measure conversion yield (Equation (1)). The equation chosen is the one presented in Furtak-Wrona's paper [22]. The stretching vibration of the alkene is visible at  $1635 \text{ cm}^{-1}$ , but the amine group, present in the acrylated allophanate oligomer, vibrates nearby. Thus, this peak was not used for the calculation. Equation (1) is calculated as follows:

$$\Pi = \left(1 - \frac{A_{\text{acryl}} \times A_{\text{ref}}^0}{A_{\text{acryl}}^0 \times A_{\text{ref}}}\right) \times 100 \tag{1}$$

where  $A_{\text{acryl}}$  and  $A_{\text{acryl}}^0$  are the absorbance of the acrylate peak of the cured film and the uncured formulation, respectively. At the same time,  $A_{\text{ref}}$  and  $A_{\text{ref}}^0$  are the absorbances of the reference peak in the cured film and the uncured formulation, respectively.

#### 2.3.2. Dynamic Mechanical Analysis Measurements (DMA)

DMA measurements were performed following the same procedure used in the first part of the study [15]. Coatings' glass transition temperatures were determined using the maximum loss modulus. The maximum loss factor (tan $\delta$ , Equation (2)) is also noted to know the end temperature of the glass transition. Cross-linking densities (CLD) were measured from the minimum of storage modulus (Equation (3), Figure 3). To be repeatable, the minimum storage modulus is taken at the temperature T<sub>g</sub> + 50 °C. As performed previously, the samples were cut with CO<sub>2</sub> laser machine (LMC-2000 from Beam Dynamic

at 500 W, Edgar, WI, USA) at 2.5 cm  $\times$  0.5 cm. Equations (2) and (3) are calculated as follows:

$$\tan(\delta) = \frac{E'' \text{ loss modulus}}{E' \text{ storage modulus}}$$
(2)

$$CLD = \frac{\min(E')}{3 \times R \times T}$$
(3)

where tan( $\delta$ ) is the loss factor, E<sup>''</sup> the loss modulus, E' the storage modulus, CLD the crosslinking density (in mol/m<sup>3</sup>), R the gas constant (in Pa.L/mol.K), and T is the temperature at T<sub>g</sub> + 50 °C (in K). CLD was measured from E', the storage modulus in the rubbery plateau at T<sub>g</sub> + 50 °C (in Pa).



**Figure 2.** FTIR spectrum of the HEMA-PETA-Ebecryl 4738 formulation ( $n^{\circ}2$ ). The red curve is the curve film, and the blue curve is the uncured formulation.



Figure 3. DMA curve indicating the glass transition temperature and the minimum of storage modulus.

## 2.3.3. Hardness Characterizations Pendulum Damping Tests

König hardness pendulum indicates surface stiffness. Good coating flexibility is important to ensure that coatings sustain wood's dimensional changes. Moreover, a high stiffness may cause coating fracture under mechanical aggressions. König pendulum hardness tester from BYK Additives & Instruments (Columbia, SC, USA) was used. Coatings were applied on glass panels according to ASTM standard D4366 [23] and to limit variability from wood substrates and ensure reproducibility. The pendulum was placed on the coating samples and tilted up to  $6^{\circ}$ . A stiff coating gives a high value of oscillations or a high damping time from  $6^{\circ}$  to  $3^{\circ}$ . At the opposite, a flexible coating absorbs the pendulum's energy, and a low value of oscillations/low damping time is thus found. Three repetitions were performed on each coating, and three coatings were tested per formulation.

#### Indentation Measurements

To quantify the hardness and elasticity of the coatings, instrumented micro-indentation measurements were performed. Four indentations on four different areas of the coatings were performed with the Micro Combi Tester (MCT3, Anton Paar, Graz, Austria) with a Berkovick diamond pyramidal tip. Three repetitions were completed per sample. The indentation parameters selected were 10 mN initial contact force, 125 mN maximum load, 500 mN/min loading rate, and the maximum load held for 5 s before unloading. The information obtained was the indentation hardness HIT and the elasticity given by the reduced Young's modulus E\*, with these two calculated using the Oliver and Pharr methodology [24].

### 2.3.4. Reverse Impact Resistance

The reverse impact has been selected to characterize the elasticity of the coatings. The variable impact tester (Elcometer 1615, Warren, MI, USA) was used with a 0.91 kg weight with the hemispherical punch. The coating on metallic substrate was placed under the falling guide, coating face down. Then, the weight fell from a certain height. The height was gradually increased until the coating broke under the impact. The value of the maximum height which the coating resist is used to calculate the reverse impact resistance following Equation (4):

Reverse impact resistance (cm/kg) = maximum height 
$$\times$$
 0.91 (4)

## 2.4. Self-Healing Characterization

The protocol followed to characterize self-healing behavior was developed in the first part of the study [15]. For each test, the coatings were applied on metallic panels to ensure repeatability. The objective of the self-healing property is to recover the appearance and mechanical properties. Two methods were used to quantify these properties: gloss measurements and scratch depth measurements.

#### 2.4.1. Self-Healing Characterization by Gloss Measurements

Abrasion and Washability Tester (Elcometer 1720, Warren, MI, USA) was used to abrade the coatings at 37 cycles/min (in agreement with standard ISO 11998, 2006). One cycle of abrasion meant one back and forth cycle with the abrasion pad. The abrasions were performed using a Scotch Brite 7447B (from 3M, Saint Paul, MN, USA) abrasion pad and a 500 g weight on it.

To quantify the gloss recovery, gloss measurements were made using the micro-TRIgloss (from BYK, Columbia, SC, USA) at 60° before abrasion, after abrasion, and after healing. A variable number of abrasion cycles were performed (from 1 to 10). In addition, healing parameters were varied to study the impact of heating on the healing efficiency. Heating times were tested from 30 min to 10 h and heating temperature from 60 °C to 100 °C. Using these measurements, the self-healing efficiency was calculated with Equation (5):

Self-healing (%) = 
$$\frac{\text{gloss}_{\text{healed coating}} - \text{gloss}_{\text{damaged coating}}}{\text{gloss}_{\text{virgin coating}} - \text{gloss}_{\text{damaged coating}}} \times 100$$
 (5)

2.4.2. Self-Healing Characterization by Scratch Depth Measurements

The Micro Combi Tester (MCT3, Anton Paar, Graz, Austria) allows to make controlled scratches, at constant and progressive load. To do so, a 200  $\mu$ m radius Rockwell C diamond tip was selected.

Scratches were first performed at a constant load of 5 N, with a scratch length of 3 mm and a scratch speed of 6 mm/min. Scratch depth was then measured with ContourGT-I profilometer (Bruker, Billerica, MA, USA). Coatings were then placed in oven at 80 °C for 2 h to evaluate their self-healing behavior. Another profilometry scan was then completed to measure the scratch depth after heating. The information of scratch depth after scratching and heating allows the calculation of self-healing efficiency, following Equation (5), and the results were compared using Tukey statistical analysis:

Self-healing efficiency (%) = 
$$\frac{\text{Depth}_{\text{damaged coating}} - \text{Depth}_{\text{healed coating}}}{\text{Depth}_{\text{damaged coating}}} \times 100$$
(6)

Secondly, progressive load scratching from 0.3 N to 8 N was applied on coatings using the same scratch length and speed parameters described above. As previously, profilometry before and after heating was performed to measure scratch depth and calculate self-healing efficiency. This test gives information about the self-healing efficiency according to scratch depth and the maximum load until self-healing behavior is observed. Again, Tukey statistical analysis was used to compare the results.

For both tests, profilometry measurements were taken in VSI mode (Vertical Scanning Interferometer), with  $10 \times$  magnification, white light source, and 1% threshold. Profilometry scans were performed from 20 µm of the back scan to 30 µm of scan length.

## 3. Results and Discussion

The reference formulation is the most efficient self-healing coating developed in the previous study [15], i.e., the HEMA–Ebecryl 4738 formulation. A variable quantity of PETA and AHPMA monomers were added to this formulation to improve the mechanical properties of the coatings and to study the impact of these monomers on self-healing efficiency. Six formulations were made as described in the Section 2, and physicochemical, mechanical, and self-healing characterization were performed on each coating.

#### 3.1. Physicochemical and Mechanical Characterization

# 3.1.1. Fourier Transformation Infrared Spectroscopy

The FTIR spectroscopy allows the calculation of acrylate groups conversion yield in the formulations following Equation (1). Conversion results and average functionality are presented in Table 3. The average functionality is the average number of acrylate functions per molecule in the formulation.

Notably, small concentrations of PETA decrease the conversion yield. On the opposite, increasing the quantity of PETA and AHPMA increases the conversion. This indicates that two parameters are influencing the conversion yield. The first one is the average functionality. A high functionality induces a fast cross-linking and gel formation, reducing more quickly the monomer mobility in the formulation. Thus, the conversion yield is reduced [25]. This was already observed in the previous study [15]. The other effect is the quantity of acrylate and methacrylate in the formulation. It is well known that methacrylates are less reactive under UV than acrylates. This is due to their higher stability, and the methyl group next to the free radical induces stability of this radical, therefore,

the methacrylates monomer has a longer induction period than the acrylates [26]. The monomer HEMA contains only one methacrylate function, PETA contains three acrylate functions, and AHPMA contains one acrylate and one methacrylate function (Figure 1). Consequently, adding a PETA monomer means adding acrylate functions that are more reactive, and it increases the conversion yield. This effect is less visible on the AHPMA formulation because it has only one acrylate, but it is still present.

n°	Monomer	Oligomer	Average Functionality	Conversion (%)
1	HEMA		1.87	$62 \pm 1$
2	90% HEMA 10% PETA		1.97	$53\pm1$
3	70% HEMA 30% PETA		2.08	$57\pm2$
4	50% HEMA 50% PETA	Ebecryl 4738	2.22	$65\pm1$
5	90% HEMA 10% AHPMA		1.98	$61 \pm 1$
6	70% HEMA 30% AHPMA		2.06	$64\pm1$
7	50% HEMA 50% AHPMA		2.13	$63 \pm 3$

Table 3. Conversion yield results measured by FT-IR spectroscopy.

3.1.2. Dynamic Mechanical Analysis

The Dynamical Mechanical Analysis (DMA) was used to measure the glass transition temperature  $(T_g)$  and the cross-linking density (CLD). All results are presented in Table 4.

n°	Monomer	Oligomer	T <sub>g</sub> (°C) = max(E″)	Max tan(δ) (°C)	CLD (mol/m <sup>3</sup> )
1	HEMA		$78\pm2$	$100\pm 2$	$3268\pm89$
2	90% HEMA 10% PETA		$75\pm1$	$98\pm1$	$2869 \pm 127$
3	70% HEMA 30% PETA		$76\pm2$	$101 \pm 1$	$3848\pm257$
4	50% HEMA 50% PETA	Ebecryl 4738	$76\pm2$	$108\pm2$	$4935\pm115$
5	90% HEMA 10% AHPMA		$74\pm2$	$97\pm1$	$3295\pm122$
6	70% HEMA 30% AHPMA		$74\pm2$	$100 \pm 1$	$4062 \pm 159$
7	50% HEMA 50% AHPMA		$75\pm1$	$105\pm1$	$4589 \pm 184$

**Table 4.** Formulations' T<sub>g</sub> and CLD measured by DMA.

The  $T_g$  measurements are not significantly different, which is explained by the similar compositions. Indeed, only a part of the monomer composition varies between the seven formulations. This could indicate that oligomers are the main factor determining the  $T_g$  value as they are a major part of the formulation. All the  $T_g$  values are between 70 °C and 80 °C, but the loss modulus is around 100 °C. If self-healing occurs after the end of the glass transition, the coating n°4 would not be used for wood application, as reaching this temperature risks overdrying the wood, creating cracks. Variations are more significant for the CLD results than the  $T_g$  results. The lowest CLD is obtained for the coating n°2, which can be explained by the low conversion yield. It is notable that increasing the quantity of PETA and AHPMA increases the CLD considerably. Indeed, PETA and AHPMA have more acrylate and methacrylate functions than HEMA (monomers structure were presented in Figure 1, and formulation composition was described in Table 2). Coatings n°3, 6, and 7 have higher CLD than coating n°1. In this study,  $T_g$  and CLD are not proportional.

## 3.1.3. Hardness

Hardness is one of the most important parameters to ensure scratch resistance. Indeed, coatings must be hard enough to resist mechanical aggression but flexible enough to sustain wood's dimensional changes. Two hardness measurements were performed, a macroscopic one and a microscopic one. The surface stiffness (macroscopic characterization) was measured using the pendulum hardness tests. The results are presented in Table 5. As shown in Table 6, indentation measurements were selected to quantify the hardness for the

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microscopic characterization. The indentation hardness, HIT, is the resistance to the plastic deformation upon loading with the indenter.

n°	Monomer	Oligomer	Hardness Pendulum (osc)
1	HEMA		$81 \pm 1$
2	90% HEMA 10% PETA		$77\pm3$
3	70% HEMA 30% PETA		$79\pm2$
4	50% HEMA 50% PETA	Ebecryl 4738	$110\pm7$
5	90% HEMA 10% AHPMA	-	$73\pm2$
6	70% HEMA 30% AHPMA		$74\pm3$
7	50% HEMA 50% AHPMA		$95 \pm 3$

 Table 5. Hardness pendulum results.

Table 6. Indentation hardness (H<sub>IT</sub>) measured by indentation.

n°	Monomer	Oligomer	H <sub>IT</sub> (MPa)	E* (GPa)
1	HEMA		$231\pm10$	$6.2\pm0.2$
2	90% HEMA 10% PETA		$243\pm8$	$6.0 \pm 0.3$
3	70% HEMA 30% PETA		$291\pm7$	$7.3\pm0.3$
4	50% HEMA 50% PETA	Ebecryl 4738	$324\pm5$	$7.2\pm0.3$
5	90% HEMA 10% AHPMA	-	$238\pm9$	$6.2\pm0.2$
6	70% HEMA 30% AHPMA		$239\pm7$	$5.9\pm0.2$
7	50% HEMA 50% AHPMA		$248\pm10$	$6.0 \pm 0.2$

The targeted hardness pendulum value for sealant wood coating is around 80 oscillations.

From the results obtained, it can be noticed that PETA induces rigidity. This is due to higher CLD observed by DMA caused by the high number of acrylate functions. The hardness value of coating n°4 is significantly higher than the other formulations. Having such high hardness is suitable for a topcoat, however, sealers are usually softer. Another observation is that a small quantity of AHPMA decreases the hardness pendulum value. A high quantity of AHPMA monomers increases the hardness because of the average functionality of the PETA monomer.

Indentations were performed on each coating to evaluate if penetration hardness impacts the self-healing efficiency. The results are presented in Table 6.

The results indicate that the presence of a second monomer in the formulation improves the resistance to plastic deformation. PETA monomers increase coating hardness because of a high CLD. In addition, increasing the quantity of AHPMA gradually enhances the HIT. The results of HIT do not follow the same tendance as pendulum hardness results. Indeed, pendulum hardness measures the damping of the friction between the pendulum and the coating.

In contrast, indentation measures the coatings' resistance to plastic deformation. That indicates that the pendulum hardness is a surface characterization instead of HIT, which is the intrinsic hardness. In both characterizations, coating n°4 is the one with the highest value.

#### 3.1.4. Impact Resistance

Reverse impact resistance gives information about the coatings' flexibility [27]. The impact of the falling ball will deform the coating in extension. The more flexible the coating is, the more it will resist the deformation under impact. The results of the reverse impact resistance are presented in Table 7.

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n°	Monomer	Oligomer	Reverse Impact Resistance (cm/kg)
1	HEMA		$16.4\pm1$
2	90% HEMA 10% PETA		$9.1\pm2$
3	70% HEMA 30% PETA		$10.9\pm2$
4	50% HEMA 50% PETA	Ebecryl 4738	$10.0 \pm 1$
5	90% HEMA 10% AHPMA	-	$15.5\pm2$
6	70% HEMA 30% AHPMA		$15.5\pm1$
7	50% HEMA 50% AHPMA		$13.7 \pm 2$

Table 7. Reverse impact resistance.

Coatings containing PETA show low impact resistance. They are also the coatings with high hardness, but this information indicates that they are stiff. The coating impact resistance is inversely proportional to the indentation hardness. This is because the stiffness, measured by reverse impact resistance, induces the coating to break under impact. At the opposite, a coating with high hardness will deform under impact, without breaking. Therefore, the higher the coating hardness is, the lower the impact resistance is. These properties are important to develop a resistant wood flooring coating. Hence, the selected coating must have optimum hardness and impact resistance value. At this stage of the study, coatings with PETA monomers are too stiff and not resistant enough to impact to be applicable on wood flooring.

The self-healing efficiency of these coatings will be studied in the following section, and it will be observed if the high stiffness and CLD inhibit the self-healing behavior.

#### 3.2. Self-Healing Characterization

## 3.2.1. Self-healing Characterization by Gloss Measurements

Gloss was used to characterize the self-healing property after abrasion on the coating. The impact of the abrasion quantity and heating parameters on the self-healing efficiency were evaluated. The number of abrasion cycles, the heating temperature, and the duration were varied. First, the results of the variation of abrasion cycles quantity are presented in Figure 4.

It is notable that the addition of PETA significantly decreases the self-healing efficiency. This is explained by the rigidity observed in the hardness and impact resistance characterizations. Indeed, the three acrylate functions induce higher CLD, which reduces the chain mobility necessary to ensure self-healing. Moreover, the alcohol groups involved in the reversible hydrogen bonds are sterically hindered, as observed on the monomer structure Figure 1. This inhibits the self-healing behavior. According to these results, the PETA formulations were eliminated for further self-healing tests.

We considered as acceptable a self-healing efficiency of 50%, as it is enough to recover the aesthetic aspect of the wood flooring coating. Some coatings ( $n^{\circ}1$ , 5) show healing efficiencies higher than 50% until seven cycles of abrasion; others ( $n^{\circ}6$ , 7) show 50% of healing was reached at five and three cycles of abrasion, respectively. On average, five cycles of abrasion were determined as the maximum abrasion quantity, which can be repaired by the self-healing behavior of these coatings. This value is the one used for the following self-healing tests.

The second parameter that was studied is the self-healing temperature. Heating was required to reach  $T_g$ , so to allow chain mobility, it was necessary to observe self-healing by rebounding. The impact of the heating temperature is presented in Figure 5.



Figure 4. Self-healing results after heating 2 h at 80 °C, varying abrasion quantity, obtained by gloss measurements.



Figure 5. Self-healing efficiency after five abrasion cycles and heating 2 h at T, obtained by gloss measurements.

These results show that a plateau in the self-healing efficiency is reached at 80 °C for most formulations. This value is slightly higher than the  $T_g$  of most of the coatings. This information indicates that observing self-healing is necessary to heat until the beginning of the glass transition. Below this temperature, the self-healing efficiency is low and not enough to recover the aspect of the coating. In addition, reaching the end of the glass transition does not improve the self-healing efficiency. This information is very important for the self-healing research field; reaching the rubbery state of the polymer is not necessary for self-healing using hydrogen bond technology, and the glass transition is sufficient to observe self-healing.

The last parameter is the heating duration. The samples were heated at 80  $^{\circ}$ C from 30 min to 10 h. The results are presented in Figure 6.



Figure 6. Self-healing efficiency after five cycles of abrasion and heating 2 h at several time, obtained by gloss measurements.

It is observable that the heating duration considerably impacts the self-healing efficiency. A plateau of healing efficiency is observable for all the coatings. For the coatings  $n^{\circ}5$  to 7, the plateau of healing efficiency is reached after 2 h of heating. After this duration, the self-healing efficiency varies within the standard deviation value. The coating  $n^{\circ}1$  is the only one showing good self-healing after only one hour of heating. For this coating, a longer heating time does not improve the self-healing behavior. In fact, the healing efficiency stagnates around 50%.

After varying the abrasion cycles and the healing parameters (time and heating temperature), it can be concluded that heating for 2 h at 80  $^{\circ}$ C is the optimum setting to observe self-healing on these acrylate coatings. In addition, the limit of these self-healing coatings is five abrasion cycles. Upon this point, the abrasions were too deep to be repaired. The hypothesis is that some polymer is removed from the coating during abrasion, so hydrogen bonds cannot be rebound.

To further understand the self-healing behavior of these four coatings, scratch depth measurements were performed with a constant and progressive load.

3.2.2. Self-Healing Characterization by Scratch Depth Measurements

As explained in the Section 2.4.2, ductile scratches at 5 N were performed, and the scratch depths were measured by profilometry. Then, the coatings were heated for 2 h at 80 °C, as determined previously. The results are presented in Table 8.

n°	Monomer	Oligomer	Scratch Depth (µm)	Depth after Heating (µm)	Self-Healing (%)	Tukey Statistic
1	HEMA		$5.3\pm0.4$	$0.2\pm0.1$	$96\pm2$	А
5	90% HEMA 10% AHPMA	Ebecryl 4738	$4.8\pm0.3$	$0.4\pm0.2$	$91\pm 5$	AB
6	70% HEMA 30% AHPMA		$4.5\pm0.2$	$0.5\pm0.1$	$90\pm2$	В
7	50% HEMA 50% AHPMA		$4.3\pm0.2$	$0.3\pm0.2$	$93\pm4$	AB

Table 8. Self-healing results obtained by scratch depth measurements for 5 N load scratches.

This characterization indicates that the four coatings have very good self-healing efficiency. Self-healing of 90% is a high value for scratch reparation at low temperatures (below 100 °C). These tests suggest that the higher self-healing efficiency is obtained for the coating  $n^{\circ}1$  and the lowest one is for the coating  $n^{\circ}6$ , with a significant difference between both. The addition of the AHPMA monomer also reduces the healing behavior very slightly. Still, there is no correlation between the AHPMA quantity and the healing efficiency, and there is no significant difference between these coatings.

To visualize the self-healing behavior, Figure 7 presents the profilometry images of the coating n°5. On the left, there are 2D and 3D images before heating. The three scratches are clearly defined, and the scratch depth is observable. On the right, the 2D image after heating for 2 h at 80 °C shows three marks instead of scratches. Scratches are almost completely healed, as indicated by the self-healing value in Table 8. Similar profilometry images are obtained for all the coatings studied, confirming that they all have high self-healing efficiency.



**Figure 7.** Profilometry images of coating  $n^{\circ}5$  after 5 N scratch (left) and after heating for 2 h at 80 °C (right).

Scratch depth measurements were also performed for progressive load scratches. Scratches from 0.3 N to 8 N were produced as described in the Section 2.4.2. An example of the scratch obtained is presented in Figure 8. The scratch depth is measured by profilometry before and after heating 2 h at 80  $^{\circ}$ C.

From these scratches, the self-healing value at the deepest point (under 8 N), as well as the maximum depth which is 100% repaired, are calculated. The results are presented in Table 9.



Figure 8. Microscopic photography of the scratch under progressive load.

n°	Monomer	Oligomer	Scratch Depth at 8 N	Self-Healing at 8 N	Tukey Statistic	Maximum Depth Repaired at 100%	Produced Under
1	HEMA		$14\pm1~\mu{ m m}$	$73\pm6\%$	В	3.9 µm	6.7 N
5	90% HEMA 10% AHPMA	Ebecryl 4738	$12\pm2~\mu m$	$77\pm6\%$	В	4.8 μm	7.2 N
6	70% HEMA 30% AHPMA		$9\pm2\mu m$	$96\pm6\%$	А	4.0 μm	6.9 N
7	50% HEMA 50% AHPMA		$11\pm1\mu\text{m}$	$68\pm5\%$	В	3.5 µm	6.4 N

Table 9. Self-healing results on progressive scratches.

The first observation is that coating  $n^{\circ}6$  presents the best self-healing efficiency for damages caused under 8 N. It is also the one with the lowest scratch depth at 8 N, explaining the high self-healing efficiency. According to the Tukey statistical analysis, the value is high enough to be significantly different from the four other coatings. Coating  $n^{\circ}7$  is the one with the lowest self-healing and the lowest maximum repaired depth but is not substantially different from the coatings  $n^{\circ}1$  and 5. These results do not correspond to the previous one in Table 8. In fact, there are several types of damages according to the load, and it is possible that the elastic–plastic ratio of the damage is not the same under 5 N and 8 N.

In addition, the maximum depth that is 100% repaired is important information to know the deepest damage possible to repair after 2 h at 80 °C. The best result is obtained for coating  $n^{\circ}5$ , which has 100% self-healing efficiency until 4.8 µm of scratch depth (obtained under 7.2 N). The scratches' profiles are presented to visualize the results (Figure 9a–d).







**Figure 9.** (a) Profiles of the scratch produced under progressive (coating  $n^{\circ}1$ ) load before heating and the same scratch after heating for 2 h at 80 °C; (b) Profiles of the scratch produced under progressive (coating  $n^{\circ}5$ ) load before heating, and the same scratch after heating for 2 h at 80 °C; (c) Profiles of the scratch produced under progressive (coating  $n^{\circ}6$ ) load before heating, and the same scratch after heating for 2 h at 80 °C; (c) Profiles of the scratch produced under progressive (coating  $n^{\circ}6$ ) load before heating, and the same scratch after heating for 2 h at 80 °C; (d) Profiles of the scratch produced under progressive (coating  $n^{\circ}7$ ) load before heating, and the same scratch after heating for 2 h at 80 °C; (d) Profiles of the scratch produced under progressive (coating  $n^{\circ}7$ ) load before heating, and the same scratch after heating for 2 h at 80 °C.

Based on this study, coatings  $n^{\circ}5$  and 6 are the ones giving the most interesting results. The self-healing efficiency at the deepest point of the scratch and the maximum of repaired depth are better than the results of the reference coating ( $n^{\circ}1$ ). Coatings  $n^{\circ}5$  and 6 have high self-healing efficiencies, and the cross-linking density has been increased compared to the reference coating ( $n^{\circ}1$ ). This is a major improvement for the development of self-healing coating for wood finishing applications.

## 4. Conclusions

In this article, self-healing technology is used to improve coating resistance and, consequently, the wood flooring lifetime. The sealer layer of a typical UV-curable finishing system was studied. The reference sealer (i.e., the HEMA–Ebecryl 4738 formulation) UV-curable acrylate formulation was modified to improve its self-healing and mechanical properties. In this article, a second monomer is added in the formulation, PETA or AHPMA, then the physicochemical and self-healing properties are characterized.

The conversion yield results, measured by FT-IR, indicated that two parameters impact the conversion. As observed previously, increasing the average functionality decreases the conversion yield as the polymeric network is rigidifying rapidly. In addition, methacrylate in the formulation reduces the conversion as they are less reactive than acrylates. The cross-linking density (CLD) is an important parameter to obtain a resistant coating and was measured by DMA. High average functionality induces a high CLD, and a low conversion yield reduces the CLD. After the mechanical characterization, self-healing parameters were studied. It has been shown that heating for 2 h at 80 °C is the best setting to ensure the self-healing of these coatings. Concerning the self-healing efficiency, the coatings containing PETA monomer led to very low self-healing as they are very stiff (confirmed by hardness pendulum and reverse impact resistance). Regarding the self-healing results by gloss measurement, the HEMA-Ebecryl 4738 coating is the one with the best self-healing efficiency. This result coincides with the scratch depth measurement after constant load. The results are different under progressive load, which confirms that the self-healing efficiency depends on the type of damage. The scratches' depth measurement suggests that the healing efficiency strongly depends on the type and depth of the damage. Coatings n°5 and 6 (90% HEMA 10% AHPMA–Ebceryl 4738 and 70% HEMA 30% AHPMA–Ebceryl 4738, respectively) are the ones giving the best self-healing results, with high mechanical

properties. In conclusion, these coatings allow the combination of self-healing and wood flooring application constraints: having a high CLD and a  $T_g$  below 100 °C.

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## References

- 1. Yin, J.; Zhu, S.; MacNaughton, P.; Allen, J.G.; Spengler, J.D. Physiological and cognitive performance of exposure to biophilic indoor environment. *Build. Environ.* **2018**, *132*, 255–262. [CrossRef]
- 2. Wilson, E.O. Biophilia; Harvard University Press: Cambridge, MA, USA, 1986; ISBN 978-0-674-04523-1.
- Nyrud, A.Q.; Bringslimark, T.; Bysheim, K. Benefits from wood interior in a hospital room: A preference study. *Arch. Sci. Rev.* 2013, 57, 125–131. [CrossRef]
- 4. Stratégie d'utilisation du bois Dans la Construction. Available online: https://afsq.org/information-foret/amenagement/gestion-forestiere/foret-publique/regime-forestier-quebecois/ (accessed on 20 July 2021).
- 5. Lamason, C.; Gong, M. Optimization of Pressing Parameters for Mechanically Surface-Densified Aspen. *For. Prod. J.* **2007**, *57*, 64–68.
- Triquet, J.; Blanchet, P.; Landry, V. Hardness of Chemically Densified Yellow Birch in Relation to Wood Density, Polymer Content and Polymer Properties. Available online: https://www-degruyter-com.acces.bibl.ulaval.ca/document/doi/10.1515/hf-2020-0 076/html (accessed on 20 July 2021).
- Blaiszik, B.; Kramer, S.; Olugebefola, S.; Moore, J.; Sottos, N.; White, S. Self-Healing Polymers and Composites. *Annu. Rev. Mater. Res.* 2010, 40, 179–211. [CrossRef]
- 8. Müller, B. Coatings Formulation; Vincentz Network: Hannover, Germany, 2011; ISBN 978-3-86630-891-6.
- 9. Zhong, N.; Post, W. Self-repair of structural and functional composites with intrinsically self-healing polymer matrices: A review. *Compos. Part A Appl. Sci. Manuf.* 2015, 69, 226–239. [CrossRef]
- Herbst, F.; Döhler, D.; Michael, P.; Binder, W.H. Self-Healing Polymers via Supramolecular Forces. *Macromol. Rapid Commun.* 2013, 34, 203–220. [CrossRef] [PubMed]
- 11. Chen, X.; Dam, M.A.; Ono, K.; Mal, A.; Shen, H.; Nutt, S.R.; Sheran, K.; Wudl, F. A Thermally Re-mendable Cross-Linked Polymeric Material. *Science* 2002, 295, 1698–1702. [CrossRef] [PubMed]
- Murphy, E.B.; Bolanos, E.; Schaffner-Hamann, C.; Wudl, F.; Nutt, S.R.; Auad, M. Synthesis and Characterization of a Single-Component Thermally Remendable Polymer Network: Staudinger and Stille Revisited. *Macromolecules* 2008, 41, 5203–5209. [CrossRef]
- 13. Jo, Y.Y.; Lee, A.S.; Baek, K.-Y.; Lee, H.; Hwang, S.S. Thermally reversible self-healing polysilsesquioxane structure-property relationships based on Diels-Alder chemistry. *Polymer* **2017**, *108*, 58–65. [CrossRef]
- 14. Boyer, D.B.; Chalkley, Y.; Chan, K.C. Correlation between strength of bonding to enamel and mechanical properties of dental composites. *J. Biomed. Mater. Res.* **1982**, *16*, 775–783. [CrossRef] [PubMed]
- 15. Paquet, C.; Schmitt, T.; Klemberg-Sapieha, J.E.; Morin, J.-F.; Landry, V. Self-Healing UV Curable Acrylate Coatings for Wood Finishing System, Part 1: Impact of the Formulation on Self-Healing Efficiency. *Coatings* **2020**, *10*, 770. [CrossRef]
- Chen, Y.; Kushner, A.M.; Williams, G.A.; Guan, Z. Multiphase design of autonomic self-healing thermoplastic elastomers. *Nat. Chem.* 2012, 4, 467–472. [CrossRef] [PubMed]
- 17. Liu, J.; Cao, J.; Zhou, Z.; Liu, R.; Yuan, Y.; Liu, X. Stiff Self-Healing Coating Based on UV-Curable Polyurethane with a "Hard Core, Flexible Arm" Structure. *ACS Omega* **2018**, *3*, 11128–11135. [CrossRef] [PubMed]

- Cortese, J.; Soulié-Ziakovic, C.; Tencé-Girault, S.; Leibler, L. Suppression of Mesoscopic Order by Complementary Interactions in Supramolecular Polymers. J. Am. Chem. Soc. 2012, 134, 3671–3674. [CrossRef] [PubMed]
- 19. Wang, Z.; Liang, H.; Yang, H.; Xiong, L.; Zhou, J.; Huang, S.; Zhao, C.; Zhong, J.; Fan, X. UV-curable self-healing polyurethane coating based on thiol-ene and Diels-Alder double click reactions. *Prog. Org. Coat.* **2019**, *137*, 105282. [CrossRef]
- 20. Fan, F.; Szpunar, J. The self-healing mechanism of an industrial acrylic elastomer. J. Appl. Polym. Sci. 2015, 132, 132. [CrossRef]
- 21. Abdallh, M.; Hearn, M.T.W.; Simon, G.P.; Saito, K. Light triggered self-healing of polyacrylate polymers crosslinked with 7-methacryloyoxycoumarin crosslinker. *Polym. Chem.* **2017**, *8*, 5875–5883. [CrossRef]
- Furtak-Wrona, K.; Kozik-Ostrówka, P.; Jadwiszczak, K.; Maigret, J.; Aguié-Béghin, V.; Coqueret, X. Polyurethane acrylate networks including cellulose nanocrystals: A comparison between UV and EB- curing. *Radiat. Phys. Chem.* 2018, 142, 94–99. [CrossRef]
- 23. ASTM D4366. Available online: https://www.astm.org/Standards/D4366.htm (accessed on 20 July 2021).
- 24. Oliver, W.C.; Pharr, G.M. An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments. *J. Mater. Res.* **1992**, *7*, 1564–1583. [CrossRef]
- Wilson, L.; Illanes, A.; Soler, L.; Henríquez, M.J. Effect of the degree of cross-linking on the properties of different CLEAs of penicillin acylase. *Process. Biochem.* 2009, 44, 322–326. [CrossRef]
- 26. Kinetic Study of Free-Radical Polymerization of Multifunctional Acrylates and Methacrylates. Available online: http://www. imaging.org/site/PDFS/Papers/1997/IST-0-4/150.pdf (accessed on 1 October 2021).
- Interpretation of ASTM Testing 2009. Endura Paint. Available online: https://www.endurapaint.com/wp-content/uploads/ pdf/astm.pdf (accessed on 1 October 2021).