

Enhancing scratch resistance of UV curable coatings for wood products

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Introduction

Wood is gaining new market shares every year in the building sector and for interior wood products^{1,2}. As beneficial effects of wood are well-known^{3,4}, growing interest for interior wood products can also be related to improvement of mechanical performances. In the case of hardwood flooring, coatings constitute an important part of the final product perception. Indeed, protection aesthetic or gloss are mostly defined by the properties of the finishing products applied on the surface.

Coatings polymerized by UV light usually have high crosslinking density compared to other curing technologies⁵. UV-coatings benefit other valuable properties such as rapid polymerization and low energy consumption, giving wood flooring manufacturers the capacity to improve their efficiency.

To enhance mechanical properties of coatings several strategies can be employed. Adding inorganic charges with high Mohs hardness (MH) such as aluminum oxide (MH = 9), silica (MH = 7), titanium oxide (MH = 7) or zirconia (MH = 6,5) led to great performance gain^{6,7}. Another interesting strategy is to improve coatings' crosslinking density⁸. As abrasion resistance of polymers depends on the density and flexibility of the network⁹, using molecules with high functionality (≥ 4) can be appealing. Generally, using reactive diluents or oligomers with high functionalities tends to increase the viscosity of the formulation and the brittleness of the coating¹⁰. Due to their unique structure, dendritic materials such as hyperbranched molecules, have high functionality while maintaining low viscosity and high flexibility compared to linear molecules¹¹.

This study investigates the photochemical and mechanical properties of UV-curable formulations containing linear reactive diluents and hyperbranched molecules. To compare the properties of linear and hyperbranched reactive diluents, formulations were prepared with oligomers of various structures, functionality and mechanical properties.

Materials and methods

Formulation

The reference formulation is composed of an epoxy acrylate oligomer (60,2 wt%, Arkema, Burlington, Canada) dispersed in tripropylene glycol diacrylate (TPGDA, SR306, 15,0 wt%, Arkema, Burlington, Canada) and 1,6-hexanediol diacrylate (HDDA, SR238, 21,8 wt%, Arkema, Burlington, Canada), a defoaming agent Ricon 130, (polybutadiene, 0,01 wt%, Cray Valley, Stratford, USA) and a photoinitiator (2-hydroxy-2-methylpropiophenone, Irgacure 1173, 3 wt%, Sigma-Aldrich, Oakville, Canada). To enhance the coating mechanical properties, a first screening amongst commercially available oligomers was made. The main targeted parameter set was the glass transition temperature (T_g), were oligomers must have a T_g between 90 and 105°C. Then by

focusing on number of reactive function, value of tensile strength and Young modulus, only four oligomers remained, mechanical properties of oligomers are presented in Table 1.

Table 1: Main properties of the selected oligomers

Name	Structure	Functionality	Tg (°C)	Elongation (%)	Tensile strength		Young Modulus		Viscosity (cP or mPa.s ⁻¹)
					psi	MPa	psi	MPa	
-	Epoxy acrylate	2	51	5,0	-	-	-	-	30000 @ 25°C
CN2203	Polyester acrylate	2	91	44,0	2300	15,86	46000	317,16	1800 @ 60°C
EBECRYL 605	Bisphenol A epoxy acrylate	2	92	7,0	8300	57,00	196000	1352	6000-9000 @ 25°C
CN104A80Z	Bisphenol A epoxy acrylate	2	93	2,0	1700	11,72	40000	275,79	22500 @ 25°C
CN9010	Aliphatic urethane acrylate	6	103	3,0	4350	29,99	88000	606,74	2650 @ 60°C

To reach an adequate viscosity for roller coater application, reactive diluents were added to the formulation until the viscosity decreases to 1000 mPa.s⁻¹ (1000 cP). Five different reactive diluents were chosen, amongst them three are linear monomers commonly used in the coating industry for their low viscosity. The two remaining are hyperbranched polyester acrylates with high functionality and low viscosity compared to linear molecules with equivalent molar mass that were selected to increase the crosslinking density of the UV-cured coatings. Their structure and main properties are summarized in Table 2. According to the reference formulation, 3 wt% of photoinitiator (2-hydroxy-2-methylpropiophenone, Irgacure 1173) were also added to the formulations.

Table 2: Main properties of the reactive diluents

Name	Structure	Functionality	Tg	Viscosity
			°C	cP
Miramer M320	Glycerine (PO) ₃ triacrylate	3	35	80-120 @ 25°C
SR238	Hexane 1,6 diol diacrylate	2	43	5-8 @ 25°C
SR306	Tripropyleneglycol diacrylate	2	62	15 @ 25°C
CN2303	Hyperbranched polyester acrylate	6	104	350 @ 25°C
CN2304	Hyperbranched polyester acrylate	18	86	750 @ 25°C

Oligomers CN2203, CN104A80Z, CN9010 and reactive diluents (monomers) SR238, SR306, CN2303 and CN2304 were provided by Arkema (Burlington, Canada), Ebecryl 605 was obtain from Allnex (Kalamazoo, USA) and reactive diluents Miramer M320 was provided by Rahn (Mississauga, Canada). To clarify formulation names, oligomers were listed from 1 to 4 and reactive diluents from A to E as presented in Table 3.

Table 3: Formulation identification

		A	B	C	D	E
		Miramer M320	SR238	SR306	CN2303	CN2304
1	CN2203	F1A	F1B	F1C	F1D	F1E
2	EBECRYL 605	F2A	F2B	F2C	F2D	F2E
3	CN104A80Z	F3A	F3B	F3C	F3D	F3E
4	CN9010	F4A	F4B	F4C	F4D	F4E

Photo- Differential Scanning Calorimetry (Photo-DSC)

Differential Scanning Calorimetry (DSC) coupled with a UV lamp was used to investigate photopolymerization kinetics as polymerization rate, conversion and induction time (i.e. time to reach 1 % of conversion). DSC compares heat flows between a sample and a reference. When coupled with a UV source, it can be used to measure enthalpies of reaction during the photopolymerization.

Analyses were carried under nitrogen or air on a DSC822e (Mettler Toledo) equipped with a Lightningcure LC5 (Hamamatsu) high pressure Mercury-Xenon lamp emitting between 240 and 400 nm. Samples of $2,5 \pm 0,1$ mg were placed in an open aluminum pan and irradiated for 60 sat 50 mW/cm². Temperature was set at 30°C. Using the heat flow measured, rate of polymerization (R_p , s⁻¹) and induction time (T_{ind} , s, i.e. time to reach 1% of conversion) were calculated according to the Equations (1) and (2).

$$R_p = \frac{(dH/dt)}{\Delta H_{theo}} \quad (1)$$

$$C_{\lambda-DSC} = \left(\frac{\Delta H_t}{\Delta H_{theo}} \right) * 100 \quad (2)$$

With $\Delta H/dt$, the heat flow per time (in J.s⁻¹); ΔH_{theo} , the theoretical heat flow for the acrylate system (in J.g⁻¹) and ΔH_t , the heat flow at a time t (in J.s⁻¹). As the formulations tested are composed of one or two difunctional acrylate monomers and an acrylate oligomer, ΔH_{theo} was calculated using the Equation (3) as follows:

$$\Delta H_{theo} = \frac{f_{m1} * x_{m1} * \Delta H_A}{MW_{m1}} + \frac{f_{m2} * x_{m2} * \Delta H_A}{MW_{m2}} + \frac{f_o * x_o * \Delta H_A}{MW_o} \quad (3)$$

With f_{m1} , f_{m2} and f_o being the functionalities of the monomers and oligomer, x_{m1} , x_{m2} , x_o , MW_{m1} , MW_{m2} and MW_o the weight fraction and molecular mass respectively of components 1, 2 and 3 and ΔH_A the polymerization enthalpy per acrylate bond (86 kJ.mol⁻¹)¹².

Confocal Raman micro-spectroscopy (CRM)

CRM is a spectroscopic technique that has already been used to investigate depth profiling of coatings, laminates or composites¹³. It allows precise depth analysis through the film as the confocal aperture is setup to gather Raman scattering from a specific laser focal sampling volume. Acrylates double bonds are consumed during photopolymerization, leading to a decrease of the acrylate absorption band intensities measured by CRM. As oxygen from the atmosphere diffuses into the polymer, its inhibition effect will affect surface conversion and deeper layers.

This method enables the determination of the thickness of the oxygen-affected layer against conversion of the total film thickness and the mean conversion. Acrylate double bonds exhibit several characteristic absorption bands (see Table 4). Depending on the formulation composition, overlapping can occur. As no significant overlap was observed in the present study, the absorption band at 1636 cm⁻¹ was chosen.

Table 4: Characteristic vibrational bands of acrylate bonds

Wavenumber (cm ⁻¹)	Attribution
810	CH=CH ₂ , twisting
1190	C-O, stretching
1405	CH ₂ , scissor deformation
1636	CH=CH₂, stretching
1720	C=O, stretching

Analyses were performed using a SENTERRA II Raman microscope (Bruker Optics Inc., Billerica, USA), equipped with a motorized table (Märzhäuser Wetzlar, Wetzlar, Germany) and an x20 lens with an 0,40 numerical aperture (Olympus). Excitation wavelength is obtained with an argon ionized laser providing 100 mW light intensity at 785 nm. As this wavelength is out of the absorption range of the photoinitiator, no post-cure can take place.

Spectra results of 4 coadditions of 5 s of analysis each, giving 20 s of data acquisition for each step to obtain adequate experimental data. Spectrum were recorded as function of depth through the film with increments of 5 µm between each acquisition.

Double bonds conversion (DBC) can then be calculated as function of depth following the variation of the peak intensity of the C=C at 1636 cm⁻¹ according to the Equation (4).

$$DBC = \left(1 - \frac{I_z}{I_0}\right) * 100 \quad (4)$$

With I_z being the peak intensity at 1636 cm⁻¹ at given depth z and I_0 the peak intensity before UV-curing.

A normalization step is also needed to avoid misinterpretation during data treatment. The C=O stretching peak at 1720 cm⁻¹, which remains unchanged during photopolymerization, was chosen. Due to the amount of data collected, treatment was done with the OPUS Software and a custom made macro command launching data treatment as extraction, baseline correction, normalization and integration for each spectrum and then exporting integration results all at once. To clarify data perception and allow transmission infrared spectroscopy (Tr-IR) comparison, mean conversion was calculated by averaging DBC for each 5 µm step over the thickness according to Equation (5),

$$\text{Mean Raman DBC} = \frac{1}{n} \sum_{i=1}^n (DBC) \quad (5)$$

Film preparation

100 µm thick films were prepared on glass and metal panels to investigate polymerization extent and mechanical properties of the formulations. All products were applied using a calibrated 4 sided applicator (BYK Gardner, Columbia, USA) at a speed of 3 m/min. Crosslinking was achieved under a medium pressure mercury lamp at two conveyor speeds, 5 and 10 m/min, under atmospheric conditions.

Lamp intensity was set at 250 mW/cm², which gives energy doses of 400-450 mJ/cm² and 250-300 mJ/cm² respectively in the UVA area at 5 and 10 m/min. Intensity and energy doses were measured with a Power Puck II radiometer (EIT, Leesburg, USA).

Pendulum Hardness

Hardness was determined according to the standardized test method ASTM D4366 for König pendulum hardness¹⁴, using a König Pendulum (BYK Gardner, Columbia, USA). This test measures the damping time of a standardized pendulum disposed on the surface of a sample. For the König method, oscillation amplitude between 6 and 3° is recorded, the softer the coating the more inertia will be absorbed and the less pendulum oscillations are measured. Minimum of three measurements at different points of the film were acquired for each UV-cured formulation.

Abrasion resistance

Abrasion resistance was evaluated using a modified version of the standardized test method ASTM D6279¹⁵. This method can be employed to characterize abrasion resistance in terms of gloss loss or retention of high gloss coatings. Coating applied on Q-panels were placed on the Elcometer 1720 Abrasion and washability tester (Elcometer Inc., Warren, USA). 3M abrasive pads (constituted of a fiber matrix and silicon carbide as mineral abrader¹⁶) were then deposited on coating surface.

To ensure that a reproducible and sufficient force is applied on the coating, a weight of 500 g was placed over the samples tested. Abrasive pads were rubbed back and forth on the coatings surface for 10 cycles at a speed of 37 cycles/min. Gloss values at 20° were recorded with a BYK micro-tri-gloss gloss meter (BYK Gardner, Columbia, USA) before and after abrasion and gloss retention was calculated using the Equation 6.

$$\text{Gloss retention} = \left(\frac{\text{Abraded gloss}}{\text{Unabraded gloss}} \right) * 100 \quad (6)$$

Results and discussion

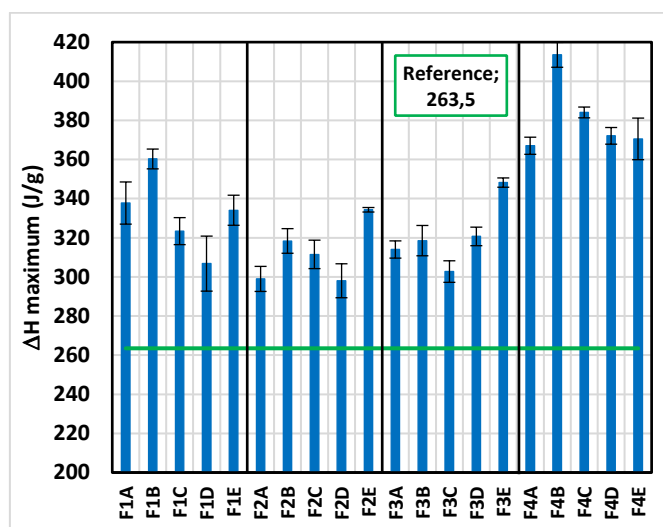
Photo-DSC

Data measured and calculated from photo-DSC analyses are reported in Figure 1a, b and c. Those figure show (a) the enthalpy maximum (ΔH maximum), (b) induction times and (c) photopolymerization rate maximum. Compared to the reference formulation, an increase in the enthalpy maximum can be observed (Figure 1a). Heat of reaction is proportional to the amount of acrylates consumed during the photopolymerization and crosslinking¹⁷. Augmentation in the heats of reaction can also be attributed to the ratio between oligomer and reactive diluents. As the viscosity of some oligomers was higher than the one of the oligomer used in the reference formulation, more diluent needed to be added, increasing the amount of reactive double bonds in the formulation.

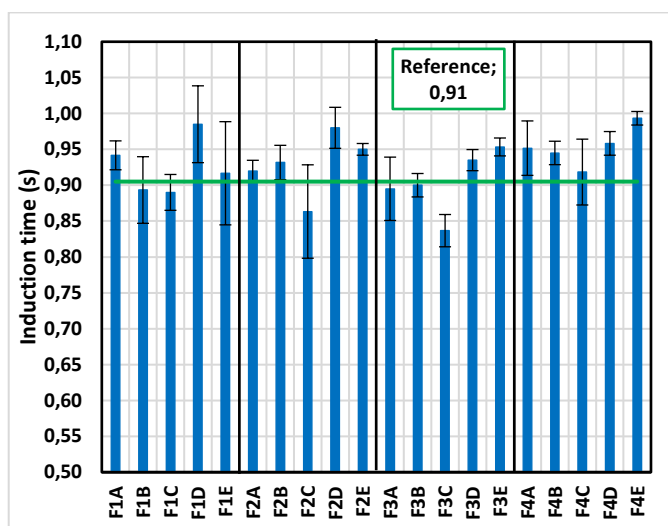
Most formulations show little to no difference in induction times compared to the reference. However hyperbranched diluents D and E had a noticeable impact, as they tend to increase induction times for almost every oligomer they were used with. In contrast, the reactive diluent C showed the lowest induction time with all four oligomers. As diluent C is the smallest molecule tested and diluent D and E are larger molecules, diffusion during the formation of the network may explain their differences.

The greatest difference between the reference and the formulations tested was obtained with the calculation of the photopolymerization rate maximum. Reactive diluent E showed a significant reduction for every formulation in which it was used. As demonstrated by other studies, those results could indicate higher crosslinking density within the coating, as E refers to the hyperbranched diluent with the highest functionality^{18,19}. During the formation of the network, propagation of the polymerization occurs until the diffusion of reactive species is limited. For well crosslinked networks, radicals' diffusion can be limited at an early stage of the polymerization, thus reducing the

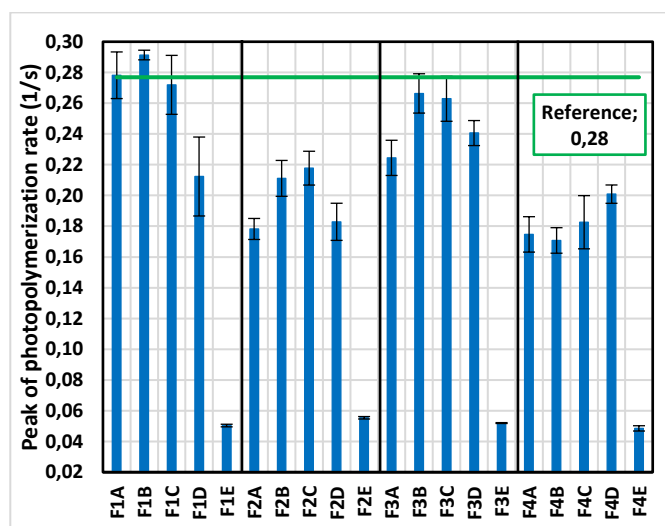
photopolymerization rate. Only the results obtained for formulations F1A, F1B, F1C, F3B and F3C (linear reactive diluents used) were found similar to the reference formulation.



(a)



(b)



(c)

Figure 1: (a) reaction enthalpy, (b) induction time and (c) peak of photopolymerization rate of the formulations

Confocal Raman Micro-spectroscopy (CRM)

As the reference formulation was first developed for its good UV-curing properties, it was expected that most formulations tested could not reach the same double bonds conversion (DBC) (see Figure 2). Moreover, as mentioned for the maximum photopolymerization rate, some oligomers and reactive diluents used have a high functionality (≥ 6), which means that even if a well crosslinked network is formed, a certain amount of unreacted acrylates double bonds remains trapped into the network. Nevertheless, it should be noticed that formulations containing the hyperbranched diluent D showed the highest DBC with almost every oligomer cured at 5 m/min with 70,4 % for

F1D, 72,4 for F2D, 81,6 for F3D and 65,5 % for F4D. Formulation F1B also showed a decent DBC with 77,7 %.

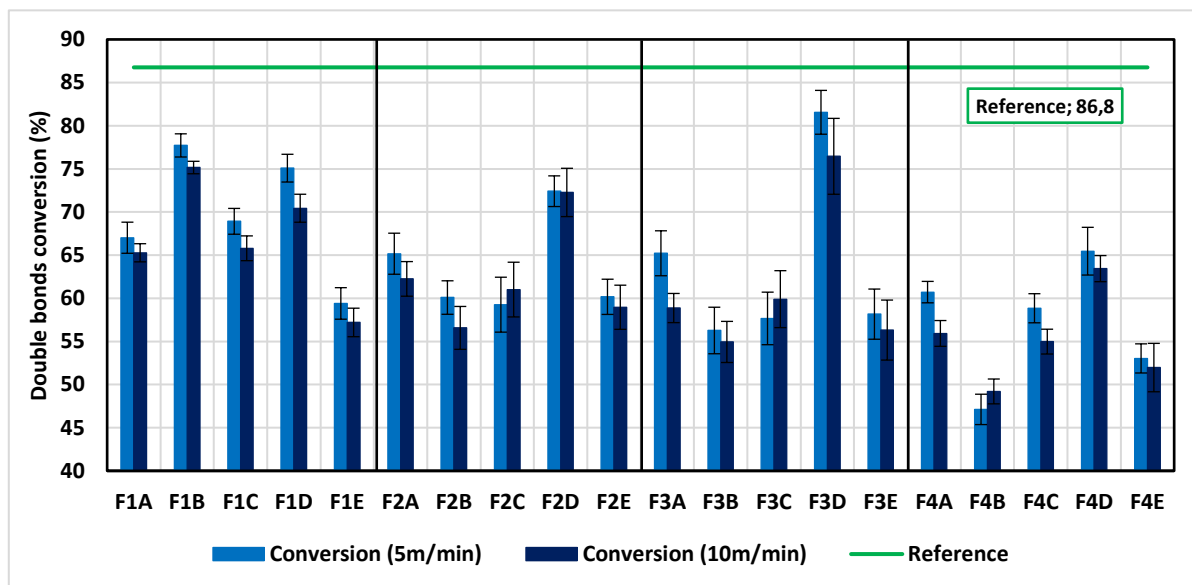


Figure 2: Double bonds conversion measured by CRM

Pendulum Hardness

Pendulum hardness results are displayed on Figure 3 for both conveyor speeds. Amongst all formulations tested almost half of them did not reach the hardness of the reference formulation. Lower pendulum hardness could be explained by several reasons. During the photopolymerization process, oligomers and monomers can have different reactivity. This will lead to a separation of the formulation components and in extreme cases to a mixture of homopolymers composed of almost only monomers or oligomers. In less extreme cases having shorter chains consisting of monomers can act as a plasticizer and reduce the hardness of the final polymer²⁰. As mentioned before, for radical polymerization, oxygen inhibition may occur, leading to formation of peroxy radicals, unable to propagate the polymerization and forming shorter polymer chains.

While the second hypothesis might be an explanation for formulations with a low DBC like F1A, F1C or F1E (with 67,0, 68,9 and 59,4 % at 5 m/min respectively), for formulations like F3D with a high DBC (81,6 % at 5 m/min) the first hypothesis could explained the result obtained.

It can also be noticed that at the opposite of formulations containing the oligomer 1, most of formulations F4 reached higher hardness than the reference. Similar results were obtained for Formulations F1B, F2B, F2C, F3B and F3C, which led to higher hardness than the reference.

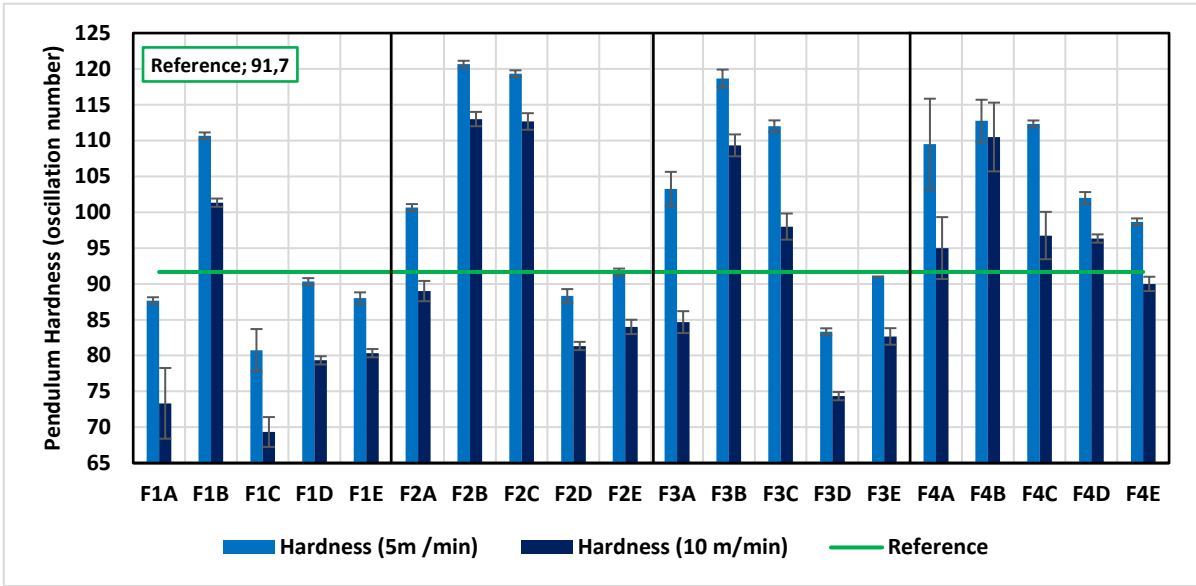


Figure 3: Pendulum hardness of formulation UV-cured at 5 m/min and 10 m/min

Abrasion resistance

Data for the abrasion resistance via gloss retention of UV-cured films are reported in Figure 4. It can be noticed that the reference formulation only retained 21,2 % of the gloss at 20°, as the oligomer composing the formulation has a lower glass transition than the other oligomers tested and a lower hardness than several formulations tested, this result could be expected. It can also be observed that beside F1C and F1E, all the formulations tested provided more than 60 % of gloss retention.

With gloss retention between 60 to 80 % formulations, F1A, F1D, F2A, F3A, F3C, F4C and F4E provided a good resistance to abrasion tests. Formulations F2B, F2D, F2E, F3D, F3E, F3A and F4D yielded very good gloss retention with over 80 % after being abraded. Formulations F1B and F4B give the best results with almost full gloss retention (over 99 %).

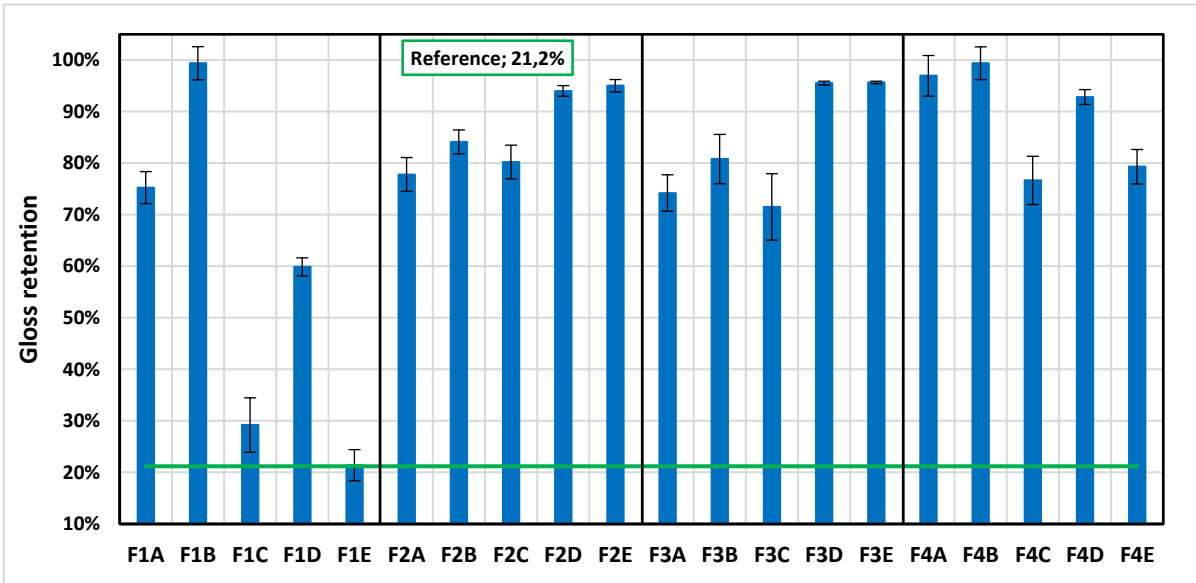


Figure 4: Abrasion resistance of formulation measured through gloss retention at 20°

Data simplification

In order to clarify data interpretation for each formulation, their UV properties (such as induction time, maximum of photopolymerization rate and double bonds conversion) along with their mechanical performances such as pendulum hardness and abrasion resistance are summarized in Table 5.

Table 5: Summary of the performances of tested formulations

<i>Tests / Formulations</i>	Induction time	Maximum photo-polymerization rate	Double bonds conversion	Pendulum Hardness	Abrasion resistance
<i>Reference</i>	+	++	++	+	--
<i>F1A</i>	-	+	-	-	+
<i>F1B</i>	+	++	+	+	++
<i>F1C</i>	+	-	-	--	--
<i>F1D</i>	--	--	+	-	+
<i>F1E</i>	-	--	--	-	--
<i>F2A</i>	-	--	-	+	+
<i>F2B</i>	-	--	--	++	++
<i>F2C</i>	++	--	--	++	+
<i>F2D</i>	--	--	+	-	++
<i>F2E</i>	-	--	--	-	++
<i>F3A</i>	-	-	-	+	+
<i>F3B</i>	+	-	--	++	++
<i>F3C</i>	++	-	--	+	+
<i>F3D</i>	-	-	++	--	++
<i>F3E</i>	-	--	--	-	++
<i>F4A</i>	-	--	--	+	++
<i>F4B</i>	-	--	--	++	++
<i>F4C</i>	-	--	--	+	+
<i>F4D</i>	--	--	-	+	++
<i>F4E</i>	--	--	--	+	+

From this table it can be noticed that only few o formulations tested had better UV-curing properties than the reference formulation. For instance only F1B showed good results in all three categories. Other formulations like F1C, F1D, F2C, F2D, F3B, F3C and F3D provided good results but only in one category, mostly induction time or double bonds conversion. As mentioned before, for most of the oligomers tested, the hyperbranched diluent D yielded the best double bonds conversion.

It can also be observed that pendulum hardness allowed a better differentiation between tested formulations. Formulations F2B, F2C, F3B and F4B reached very good hardness with over 110 oscillations. Formulations F1B, F2A, F3A, F4A, F4C, F4D and F4C also showed better hardness than the reference formulation.

Almost every formulations tested had better resistance to abrasion than the reference formulation, with F1B and F4B over 99 % of gloss retention. Most of the formulations tested in this study reached 70 % or more of gloss retention. Hyperbranched reactive diluents used in formulations F2D, F2E, F3D, F3E and F4D provided very good results with over 90 % of gloss retention when abraded.

Conclusions

Some of the best mechanical properties were obtained with oligomer F4, this may indicate that enhancing density of the network by using components with high functionality could be an

interesting strategy. Usually oligomers with high functionality tend to have high viscosities and also tends to provided brittle coatings. They also contribute to form networks with a relative amount of unreacted bonds trapped in the network. Using hyperbranched molecules may be a good strategy to keep viscosity low enough to be applied, maintain flexibility within the coating and also allow better UV-curing. In order to validate this hypothesis, more specific mechanical properties could be considered, as elongation at break, tensile strength or crosslinking density of formulated coatings.

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