WOOD COATING BY UV POWDERS

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Many wood-based panels are nowadays used in the furniture industry. Their coating is of high interest to ensure high protection properties and decoration features. UV powders recently emerge among the current existing technologies as an alternative to coat wood panels due to the following advantages: they are environmentally friendly, based on 100% solid formulations, their curing process is fast and operated at relatively low temperature, which fully preserves wood structure. Polymerization of UV powders is monitored by Real Time-FTIR under temperature control. The influence of temperature on reactivity is highlighted. Characteristics of UV powder resins, particularly molecular weight and viscosity in melted state, are related to reactivity parameters. The influence of additional multifunctional monomers within the formulations is afterwards investigated. Finally, Dynamic Mechanical Analysis is performed to determine glass transition temperature, crosslinking density and Young's modulus of the final coatings. Resistance to scratch and methyl ethyl ketone (MEK) is evaluated as well.

Keywords: wood-based panels, UV powders, crosslinking density, Young's modulus, flexibility, scratch and solvent resistance

INTRODUCTION

Wood and its derivatives are largely used in the furniture industry. The applications on medium-density fiberboards (MDF), particleboards, oriented strand boards (OSB) or plywood panels have been constantly growing up for a few years. Wood coating is of high interest as it ensures high resistance over time and offers aesthetic properties. Nevertheless, operating on wood is not a trivial process for many reasons. Wood is a sensitive material, it may release extractives[1,2] and undergo dimensional variations (cracks) in time and under specific conditions (temperature, humidity and light). Such factors may strongly affect the protective/decorative coatings. Nowadays, a number of coating technologies are known (solvent-based, water-based, high solids, UV liquid formulations, thermal powders and UV powders). UV powders appear as a promising alternative technology to coat wood-based panels, as they are environmentally friendly (no emission of volatile organic compounds), the curing process is fast (takes no longer than a few minutes) and the working temperature is low (maximum 120 °C). The curing process of UV powders generally allows preparing smooth crosslinked finishes.[3-5]

UV powders are 100% solid formulations, generally based on unsaturated (meth)acrylate polyesters and urethane (meth)acrylate resins, photoinitiators and additives (pigments or fillers). UV powders are industrially deposited at the wood surface, using either corona discharge or triboelectric electrostatic spray techniques. The curing process is performed in two distinct stages. Melting of the UV powder is first performed by heating under IR and/or by convection above the glass transition or fusion temperature of the resin, depending on its crystallinity. Next, UV irradiation allows photopolymerization of the system, following the three different steps of initiation, propagation and termination. First, light is absorbed by the photoinitiator leading to its cleavage and generation of radicals able to initiate the polymerization by their addition to the acrylate oligomer double bond. Then, the propagation step leads to the growth of polymer

radical chains. Finally, the reaction usually ends up by the recombination or disproportionation of the radical chains. However, another termination mechanism is also possible, leading to radical polymer chains trapping within the 3D crosslinking network (occlusion).[6] The reactivity of the systems is evaluated by the determination of the final conversion of monomers into polymers, and the polymerization rate. Conversion affects the final properties of the coatings.

The performance of the coating also depends on the quality of powder deposition, which is related to many features of the wood-based panels: density, thickness, humidity or roughness. Typical drawbacks are poor adhesion to the substrate, bubbling, blistering, heterogeneities, high final roughness, cracking or coloration. High thickness is generally related to low density and consequently low conductivity. Furthermore, humidity impacts on panel conductivity as well and should be preferentially comprised between 6-11%. Finally, high panel roughness generally leads to heterogeneous deposition of UV powders and final coating. It is thus necessary to preliminarily sand the surface to reach sufficient smoothness before UV powder deposition.

The present paper aims to present the UV curing process and the characterization of UV powder coatings. First, the reactivity of UV powders is investigated as a function of temperature (determination of polymerization rate and conversion). The nature of the resin and its impact on reactivity are also discussed. Relationships between molecular weight and chain length, viscosity in melted state and molecular mobility are established. Finally, the properties of UV powder coatings are evaluated by performing dynamic mechanical analyses in tension mode. Glass transition temperature (T_g), crosslinking density (X_c) and Young's modulus (E) are measured. Resistance to scratch and solvent was also determined.

EXPERIMENTAL
UV powder formulations

A first series of experiments is based on two model formulations A and B. Formulation A is a commercial urethane diacrylate solid resin (resin A - M_n: 2000 g·mol^{-1}, T_g: 56 °C) mixed with 2 wt% Irgacure 2959 as photoinitiator (Ciba Specialty Chemicals). Formulation B is a mixture of a commercial polyester dimethacrylate solid

resin (resin B - M_n: 6000 g·mol^{-1}, T_g: 51 °C) with 2 wt% Irgacure 2959.

Then, a second series of experiments is based on formulations including resin A or B with additional multifunctional acrylate monomers: M1 – a diacrylate, M2 – a tri-acrylate, and M3 – a tetra-acrylate. The addition of the multifunctional monomers to the resin is based on the ratio 20/80 wt% (acrylate monomer/solid resin).

Characterization techniques
RT-FTIR fitted with an environmental cell

The reactivity of the formulations was followed in real time with a RT-FTIR set-up (Vertex 70, Bruker Optics) equipped with an environmental cell (Analysa-LTS350 – Linkam Scientific Instruments). After a first 5 minutes step in isothermal mode (temperature selected between 50-110 °C), melted samples were irradiated under UV light (Hg-Xe lamp – Hamamatsu) for 120 seconds (irradiance: 66 mW·cm^{-2}). The disappearance of the (meth)acrylate IR band at 810 cm^{-1} was observed during UV irradiation. Conversion was measured according to Equation 1, and plotted *vs.* irradiation time.

$$Conversion = 1 - \frac{A_t}{A_0} \qquad (1)$$

where A_0 and A_t – the areas of IR band attributed to (meth)acrylate function at time t = 0 and time t.

Preparation of coatings

Large-scale samples were prepared to perform DMA, scratch and solvent tests. Curing was achieved under IR/UV conveyor (Qurtech) by a first melting step under IR lamps (Solaronics) followed by a second irradiation step under microwave lamp equipped with an H bulb (Fusion). The temperature reached during the first step is of about 110 °C. The light dose received by the sample during the second step is of 1.312 J·cm^{-2}.

Analysis of thermomechanical properties

A first set of experiments was performed by DMA (Q800 – TA Instruments) in tension mode (10 μm amplitude and 1 Hz frequency) under a temperature ramp (0-200°C). Tan Delta (ratio loss modulus E''/storage modulus E') was followed *vs.* temperature. The maximum of Tan Delta peak is attributed to the glass transition temperature (T_g). To determine the crosslinking density (X_c), E' was determined on the rubbery plateau and Equation 2 was applied.[7-9]

$$X_c = \frac{E'}{3\rho RT} \qquad (2)$$

where ρ is the material density at T, R – the gas constant, T – the temperature on the rubbery plateau and E' – the storage modulus on the rubbery plateau.

Then, stress-strain measurements were performed at 25 °C to determine Young's modulus (E), which is related to the stiffness of the material.

Resistance tests towards scratch and solvent

Cured samples were subjected manually to 5 double rubs with a steel wool pad under constant load (500 g). The loss in film transparency after the test, determined at 60° angle by a glossmeter (Byk Gardner), was regarded as a measure of scratch resistance. Any transparency loss was linked to a decrease in crosslinking density of the polymer network.

Cured films were fully immersed into methyl ethyl ketone (MEK) for 1 hour, and then dried at 110 °C for 2 hours until constant mass. Any weight loss was attributed to poor crosslinking.[10]

RESULTS AND DISCUSSION
Influence of temperature on the curing process

The optimization of the melting step is of most importance to guarantee high quality of the final coatings. Indeed, temperature impacts on viscosity in melted state and consequently on reactivity.[3] To investigate this effect, formulation A was melted at different temperatures selected from 50 to 110 °C in the RT-FTIR set-up, then the photopolymerization step was performed under UV light (constant irradiance) (Figure 1).

At 50 °C, near the resin A glass transition temperature ($T_g = 56$ °C), the system is still solid and almost no polymerization occurs. By increasing temperature, viscosity is lowered offering higher molecular mobility. The monomer units and the growing chains can move more easily, they react together or with the radicals resulting from the photoinitiator photolysis. Higher reactivity can therefore be achieved: polymerization rate (which corresponds to the slope of the kinetic curve) and final conversion are increased. Full conversion can be achieved after only 40 seconds with a temperature of 110 °C and irradiance of 66 mW·cm^{-2}.

Influence of resin nature on the curing process

The molecular weight of the resin also shows a strong influence on the reactivity. Indeed, molecular weight impacts on chain length and consequently on viscosity in melted state. To highlight this phenomenon, reactivity of formulation B at 110 °C was compared to reactivity of formulation A (Figure 2).

At the same curing temperature (110 °C), formulation B clearly exhibits lower reactivity than formulation A. As resin B possesses longer chains than resin A, its viscosity in melted state is higher. The lower molecular mobility leads thus to lower reactivity. In addition, as both resins A and B are difunctional, longer chains result in lower molar concentration in (meth)acrylate functions. Moreover, the methacrylate groups of resin B generally exhibit lower reactivity than acrylate groups.[11] All these parameters contribute to lower reactivity of formulation B.

Coatings with increased resistance properties
Thermomechanical properties

Table 1 presents the results obtained by DMA.

Table 1
Properties of final coatings: conversion, T_g, X_c and E at 25 °C

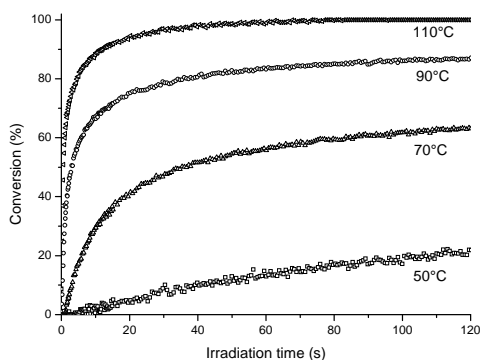| Samples	Formulations	By FTIR	By DMA Tan Delta vs. T	By DMA E' vs. T	By DMA Stress vs. strain
		Conversion (%)	T_g (°C)	X_c (mol/g) x 10^3	E (MPa) at 25°C
1	A	91	148	0.50	1042
2	A + M1	91	149	1.29	1112
3	A + M2	80	160	1.30	1458
4	A + M3	76	164	2.25	1631
5	B	60	95	0.23	912
6	B + M1	87	103	0.70	800
7	B + M2	75	114	1.61	725
8	B + M3	61	114	2.54	849

Figure 1: Influence of temperature on the curing process of formulation A (irradiance: 66 mW·cm^{-2})

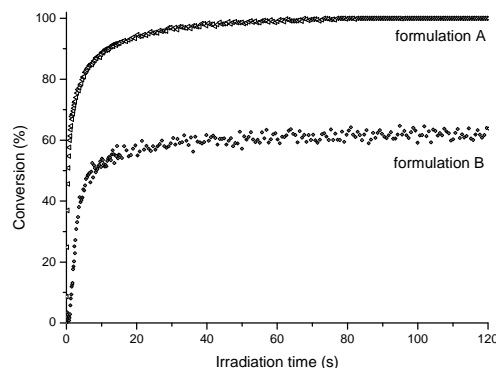Figure 2: Influence of resin nature on the curing process (T: 110 °C, irradiance: 66 mW·cm^{-2})

Independently of the resin (A or B), the addition of multifunctional monomers (M1, M2, M3) allows to build more highly crosslinked networks despite some early vitrification (limitation of conversion). Crosslinking density (X_c) is increased. As chain length between two crosslinking knots is shorter, mobility is thus reduced leading to materials with higher glass transition temperature (T_g).

Differences between properties of samples 1-4 and samples 5-8 are related to the different resins, respectively resin A and resin B. Differences in X_c tend to disappear by the addition of the multifunctional monomers: while X_c is lower for sample 5 *vs.* sample 1 (respectively 0.23 *vs.* 0.50 x 10^{-3} mol/g), it tends to similar value for sample 8 *vs.* sample 4 (respectively 2.54 *vs.* 2.25 x 10^{-3} mol/g).

The increase in X_c confirms the formation of highly crosslinked structures and, as a consequence, an effect on the resistance properties can be expected.

Scratch resistance

Figure 3 shows gloss reduction as a measure of scratch resistance.

Increasing the crosslinking density offers a better scratch resistance: gloss reduction is significantly limited for all samples based on resin A or B. However, it should be mentioned that before any scratching, samples 1-4 based on resin A were all glossier than samples 5-8 based on resin B, which exhibited a whitish colour. Therefore, a higher gloss reduction is observed for samples 1-4 (from 59 to 21%) *vs.* samples 5-8 (from 37 to 13%).

Solvent resistance

Figure 4 shows weight loss as a measure of MEK resistance.

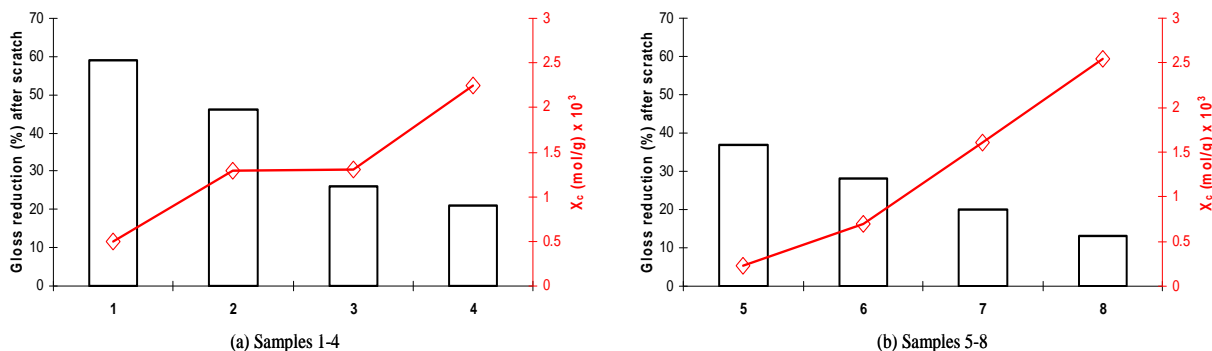(a) Samples 1-4

(b) Samples 5-8

Figure 3: Influence of crosslinking density (right Y axis) on gloss reduction after scratch (left Y axis) for samples 1-4 (a) and samples 5-8 (b)
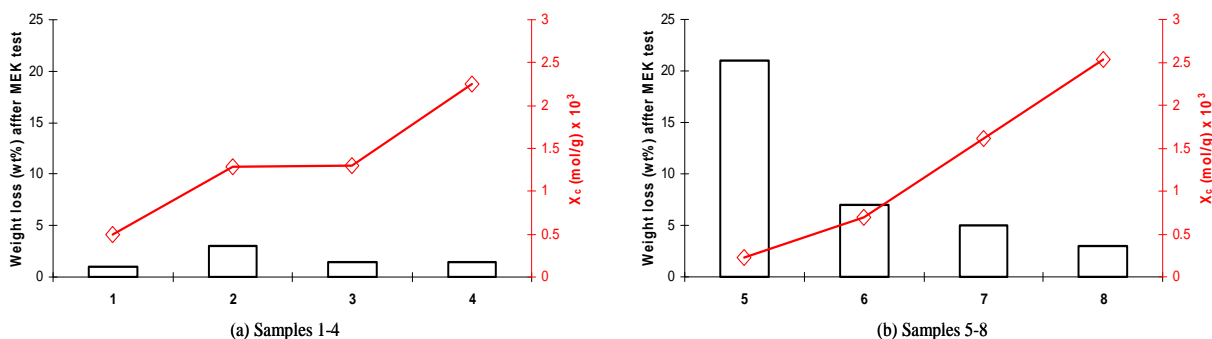
Figure 4: Influence of crosslinking density (right Y axis) on weight loss after MEK test (left Y axis)
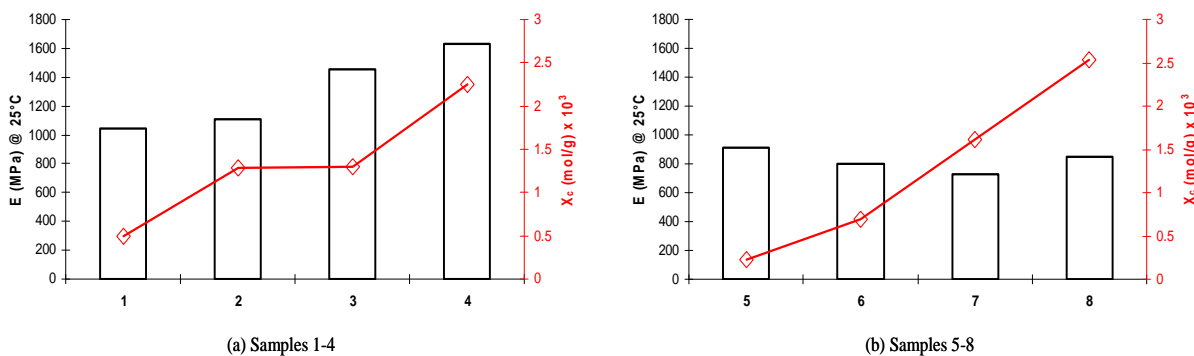for samples 1-4 (a) and samples 5-8 (b)

Figure 5: Influence of crosslinking density (right Y axis) on Young's modulus (left Y axis)
for samples 1-4 (a) and samples 5-8 (b)

On the one hand, samples 1-4 (all based on resin A) show low weight loss after immersion into MEK and almost no difference is observed among them. On the other hand, a different behaviour is noticed for samples 5-8 (based on resin B). Sample 5 (based only on resin B) is highly dissolved in MEK (21 wt%). Due to the long chains of resin B, sample 5 is weakly crosslinked. Moreover, it still possesses 40% (meth)acrylate groups, which did not react. Therefore, unpolymerized chains that are trapped within the weakly crosslinked network can be easily dissolved in MEK. The addition of multifunctional monomers (M1, M2, M3) to resin B leads to the formation of more resistant samples with a higher X_c. Even if reactive groups are still remaining in large quantity (up to 39%), the highly crosslinked network guarantees efficient trapping and ensures low dissolution in MEK. High resistance to MEK is thus achieved.

Stiffness

When coating wood-based panels, sufficient flexibility of the coatings may be required to avoid any cracking due to dimensional variations of the substrates. Young's modulus (E), which corresponds to the modulus of elasticity, is thus an important parameter to control. The higher is E, the higher is stiffness. E values for the different coatings discussed are presented in Table 1, and Figure 5 shows the relation between E and X_c.

The addition of multifunctional monomers (M1 M2, M3) to resin A leads to an increase in E from 1042 to 1631 MPa. E and X_c exhibit the same increasing trend. Highly resistant materials exhibiting high stiffness are achieved.

For samples 5-8 based on resin B, E remains approximately constant (725-912 MPa). Relatively low conversion (60-87%) and T_g (95-114 °C) are likely responsible for this low E.

Although crosslinking density increases, a relatively high flexibility is preserved; this could be advantageous when coating panels suffering from important dimensional variations. Indeed, sufficient flexibility would permit to follow dimensional variations of the substrate without cracking, thus ensuring a long life to the protective/decorative coating.

CONCLUSION

UV powders are environmentally friendly. Thanks to their fast curing process operated at low temperature, they are adapted for the coating of wood-based panels, such as MDF or plywood. To optimize the quality of UV powder deposition by electrostatic spray and the quality of final UV powders coatings, it is required to control density, thickness, humidity and roughness of the panels. The effect of temperature on reactivity has been highlighted: high polymerization rate and final conversion were achieved with a temperature increase of up to 110 °C. It was also shown that polyester or urethane (meth)acrylate resins, with different backbones and molecular weights, led to different reactivities and final properties. However, the differences in properties were levelled off between polyester and urethane (meth)acrylate based coatings when incorporating multifunctional acrylate monomers. Highly crosslinked materials with high T_g were formed, exhibiting high resistance towards scratch and solvent. Finally, polyester methacrylate based samples were shown as more flexible than urethane acrylate based samples. Depending on the final application and on the specific wood substrate, flexible coatings may be preferred to ensure durable protective and decorative functions without cracking.

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