

UV Powders for Wood Coatings

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UV powders are generally based on unsaturated (meth)acrylate polyesters and urethane (meth)acrylates, photoinitiators and additives (pigments or fillers). All compounds are solids, which make the formulations environmental friendly.

The objective of this work is to correlate the formulation's characteristics with the photochemical process and the final coatings' properties. The influence of additional acrylate monomers within the formulations is highlighted. Real Time Fourier Transform Infrared (RT-FTIR) spectroscopy fitted with an environmental cell is used to follow the reactivity during the photopolymerization under temperature and atmosphere control. Dynamic Mechanical Analysis (DMA) is performed to estimate the crosslinking density of the final materials.

Introduction

The technology of UV powders has grown in recent years. It's an industry that fulfills environmental mandates for the reduction of volatile organic compounds (VOC). In addition, their

fast curing process, operated at low temperatures, permits applications on wood-based panels such as medium-density fiberboards, oriented strand boards or plywood panels.¹⁻³ Wood substrates are largely used in the furniture market, but their curing is not a trivial process because they are highly heat-sensitive materials and can undergo dimensional variations or release extractives.³⁻⁵

UV powders are 100% solid formulations, generally based on (meth)acrylate resins, photoinitiator systems and different additives. The most frequently used resins exhibit a low functionality of (meth)acrylate reactive groups to limit shrinkage phenomenon. The introduction of commercial photoinitiators developed for conventional UV-cured technology is generally reported in UV powder formulations. However, no particular additional development was performed in this area. Industrially, UV powders are classically applied by electrostatic spray—either corona or triboelectric. Consequently, the substrate surface must be sufficiently conductive to ensure a good adhesion of the powder.

TABLE 1

Resins characteristics

Resin	Nature	Functionality	M_n (g·mol ⁻¹)	T_g (°C)	Viscosity at 110°C (Pa·s)
Resin A	Urethane acrylate	2	2,000	56	25
Resin B	Polyester methacrylate	2	6,000	51	700

TABLE 2

Formulations composition

Formulation	Composition	wt%	(Meth)acrylates concentration (mol·L ⁻¹)
A0	Resin A	100	1.1
A1	Resin A / HDDA	80 / 20	3.1
A2	Resin A / TMPTA	80 / 20	3.4
A3	Resin A / SR295	80 / 20	3.6
B0	Resin B	100	0.2
B1	Resin B / HDDA	80 / 20	2.4
B2	Resin B / TMPTA	80 / 20	2.7
B3	Resin B / SR295	80 / 20	3.0

The curing process is then divided into two distinct steps. The first step leads to a homogeneous melted film by operating above the glass transition or fusion of the resin, depending on its crystallinity. No polymerization occurs during this heating time and sufficient molecular mobility may be reached before the light activation. Moreover, the temperature required for melting does not generally exceed 120°C, which prevents any degradation of wood substrates. The second stage consists of photopolymerization and is achieved under irradiation within a few minutes or even seconds, leading to the formation of smooth crosslinked finishes (no orange peel effect).¹⁻³

Because customers in the furniture market are looking for high-resistant layers (high chemical and physical properties) while operating with a low thermal energy and rapid cure process, they are interested in developing UV-powder systems and establishing relations between structure, reactivity and final properties. This study focuses on increasing the crosslinking degree and evaluating its impact on the resistance properties of final UV powder coatings. To this end, we incorporated three liquid-acrylate monomers of different functionality into the formulations. RT-FTIR fitted

with an environmental cell was used to monitor photopolymerization reaction under temperature control. The influences of both the concentration in reactive functions and the functionality of additional monomers were assessed. Finally, thermomechanical properties, crosslinking density and resistance to solvent of UV-cured powder coatings were determined.

Experimental

Materials

UV-powder formulations were based on two solid resins provided by AkzoNobel—one urethane diacrylate and one polyester dimethacrylate. Table 1 lists their main characteristics.

To evaluate the influence of increasing (meth)acrylates concentration and functionality, three acrylate monomers were incorporated into UV-powder formulations—hexanediol diacrylate (HDDA from Cytec), trimethylolpropane triacrylate (TMPTA from Cytec) and pentaerythritol tetra-acrylate (SR295 from Sartomer).

Formulations

Acrylate monomers were blended with solid resins. Then 2 wt% of Irgacure 2959 from Ciba Specialty Chemicals were added to these mixtures (Table 2).

To ensure good homogeneity when extrusion is not possible, the selected experimental method consisted of dissolving the formulation in chloroform (CHCl₃ from Carlo Erba Reagents). Once formulations have been applied on the substrate, a preheating step (at 110°C for 20 minutes) permitted the solvent evaporation from the films. Curing of the films, 60 μm thick, were then performed under IR and UV radiations.

Study of the Photopolymerization Process

Real Time Fourier Transformed Infrared spectroscopy (RT-FTIR)

Reactivity of formulations deposited on a silicon wafer was followed using Vertex 70 RT-FTIR setup (Bruker Optics) fitted with an environmental cell (Linkam Scientific Instruments Analyza-LTS350), ensuring temperature control. Spectra were recorded with a time resolution of 0.11 second and a 4 cm⁻¹ spectral resolution. After 5 minutes isothermal mode (temperature selected between 50° and 110°C), melted samples were irradiated 80 seconds (66 mW×cm⁻²) using a Lightningcure™ LC8 (L8251 Hamamatsu) equipped with a mercury-xenon lamp (200 W).

Conversion of (meth)acrylate functions was determined by following

810 cm⁻¹ bond versus irradiation time. To counterbalance any error due to eventual thickness variation, the conversion calculation required the following of a reference band, nonreactive under UV (3330 cm⁻¹ urethane band or 1580 cm⁻¹ polyester band). The maximum polymerization rate ($R_{p \text{ max}} / M_0$) was evaluated with M_0 equal to the initial concentration in (meth)acrylate functions.

Formula 1

Conversion formula

$$\text{Conversion}(\%) = \left(1 - \frac{A_{810}^t}{A_{810}^{t_0}} \times \frac{A_{ref}^{t_0}}{A_{ref}^t} \right) \times 100$$

$A_{810}^{t_0}$ and A_{810}^t are the areas of the 810 cm⁻¹ band, respectively, at the initial time and at time t; $A_{ref}^{t_0}$ and A_{ref}^t are the areas of the reference band, respectively, at the initial time and at time t.

Resin—Nature and Reactivity

As shown in Table 3, B0 reactivity is clearly lower than A0 reactivity at the same curing temperature (110°C).

These results are linked to a lower molecular mobility due to longer chains (higher M_n) and higher viscosity at melted state of resin B. In addition, as both resins A and B are difunctional, longer chains result in lower molar concentration in (meth)acrylate functions. Finally, the methacrylate groups of resin B exhibit lower reactivity than the acrylate groups of

resin A, due to the methyl substituent on the methacrylate double bonds slightly decreasing the mobility.⁶

Temperature—Viscosity at Melted State and Reactivity

Effect of the temperature was investigated by following the photopolymerization of formulation A0 for different temperatures from 50° to 110°C. At 50°C, near the resin glass transition temperature, the system is still solid and almost no polymerization occurs. By increasing the temperature, viscosity is lowered, thus offering higher molecular mobility. The monomer units and the growing chains can move more easily and, thus, react together or with the radicals resulting from the photoinitiator photolysis. Higher reactivity can, therefore, be achieved as shown in Table 4—inhibition time reduced to zero seconds, increased polymerization rate and higher conversion.

For industrial applications performed on wood-based panels, high interest exists in reducing the working temperature in order to preserve the wood structure and not induce parasite phenomena (such as degassing or extraction of phenolic compounds).^{4,5} Therefore, a temperature between 70° to 90°C may be preferred. In addition, reducing the temperature would have a beneficial impact from both an environmental and economical aspect.

As reactivity of A0 formulation stays quite low at 70°C, the following section tries to highlight the interest for increasing (meth)acrylates concentration and functionality in order to achieve sufficient reactivity at such a moderate temperature.

Concentration in (Meth)acrylates and Functionality—Reactivity

Whatever the solid resin, the addition of the acrylate monomers allowed an enhanced polymerization

TABLE 3

Effect of resin nature on photopolymerization (curing temperature of 110°C)

Formulation	Conversion (%) after 80 s	$R_{p \text{ max}} / M_0 \times 100 \text{ (s}^{-1}\text{)}$
A0	100	112
B0	59	11

TABLE 4

Effect of temperature on photopolymerization (curing temperature varying from 50 to 110°C)

Formulation	Temperature (°C)	Viscosity (Pa·s)	Conversion (%) after 80 s	$R_{p \text{ max}} / M_0 \times 100 \text{ (s}^{-1}\text{)}$	Inhibition time(s)
A0	110	25	100	112	0
A0	90	250	85	37	0
A0	70	17,000	59	5	1.4
A0	50	no value*	17	0.2	9.3

*The resin is still solid.

TABLE 5

Effect of (meth)acrylates concentration and functionality on photopolymerization (curing temperature of 70°C)

Formulation	Conversion (%) after 80 s	$R_{p\max} / M_0 \times 100$ (s ⁻¹)
A0	59	5
A1	65	28
A2	67	30
A3	57	33
B0	47	3
B1	68	10
B2	68	13
B3	57	10

rate but a limited increase in the final conversion was observed (see Table 5).

The incorporation of the tetra-acrylate even led to vitrification phenomenon. It is assumed that some reactive sites may thus be trapped into the built crosslinked network and result in microgels formation.⁶ As such, heterogeneous structures may affect coating quality. The next part will try to evaluate crosslinking density and resistance properties.

Characterization of the Crosslinked Network

Samples Preparation

Larger scale samples were required for DMA analysis and the MEK test. Curing was performed under IR/UV conveyor (Qurtech):

- 10 pass at 5 m×min⁻¹ under IR lamps (5 Solaronics 4 kW lamps),
- 1 pass at 10 m×min⁻¹ under Fusion microwave lamp equipped with an H bulb (0.37 s; 1.312 J×cm⁻²).

Dynamic Mechanical Analysis (DMA)

Storage modulus (E') and tan delta (ratio between loss modulus E'' and storage modulus E') of free films (30 mm x 5 mm) were followed versus temperature from 0° to 200°C (3°C×min⁻¹) within Q800

TA Instruments. Experiments were performed in tension mode with 10 μm oscillation amplitude and 1 Hz frequency. To evaluate crosslinking density, the average molecular weight between crosslinks (M_c) was determined according to Formula 2. Both parameters are inversely correlated.

Formula 2

M_c formula

$$M_c = \frac{3\rho RT}{E'}$$

ρ is the material density at T (kg×m⁻³), R is the gas constant (8.314 J×mol⁻¹×K⁻¹), T is the temperature on the rubbery plateau (K) and E' is the storage modulus on the rubbery plateau (J×m⁻³).

Methyl Ethyl Ketone (MEK) Test

Free films (15 mm x 15 mm) were deep into MEK for one hour, and then dried at 110°C for two hours until constant mass.

Concentration in (Meth)acrylates and Functionality: Crosslinking Density and Resistance Properties

Table 6 gathers analyses results of the cured coatings—conversion, thermomechanical properties, M_c and resistance to solvent.

It should first be noted that the IR/UV process allows reaching

higher final conversion compared to the previous results thanks to high working temperature (near 110°C), broad irradiation spectrum, and high irradiance. However, some conversion levelling off due to vitrification can still be observed with the addition of the multifunctional monomers.

Apart from this phenomenon, increasing the concentration in (meth)acrylates and the functionality results in building a higher crosslinked network. Chain length between two crosslinking knots is shorter (lower M_c). Mobility is thus reduced, leading to materials with a higher glass transition temperature (T_g).

The combination of high T_g with the presence of remaining reactive functions (not 100% conversion) makes it a viable process for coated wood-based panels. While the thermo-mechanical properties are improved, sufficient flexibility is ensured to follow the eventual dimensional variations of the wood (under time or environmental conditions).

The films that only contain resin A or resin B exhibit high difference in M_c (respectively, 1,992 versus 4,352 g×mol⁻¹). The high M_c due to resin B is linked to long chains (M_n of 6,000 g×mol⁻¹) and the structure of the resin B skeleton. However, this significant difference in M_c tends to disappear with the addition of the multifunctional acrylate monomers and formation of high crosslinked networks. Finally, it is possible to get similar M_c for coatings based on resin A or resin B (respectively, 445 versus 393 g×mol⁻¹).

It should also be noted that coatings based on resin B, which exhibit methacrylate functions, and acrylate monomers show a unique value of T_g . This point confirms the copolymerization process between resin B and the acrylate monomers.

The decrease in M_c confirms the formation of high crosslinked

TABLE 6

Effect of (meth)acrylates concentration and functionality on the formation of crosslinked network and resulting properties

Formulation	Conversion (%)	T _g (°C)	E' (MPa) at 198°C	M _c (g·mol ⁻¹)	Weight loss (%) into MEK**
A0	91	148	6	1,992	1
A1	91	149	15	778	3
A2	80	160	15	768	1.5
A3	76	164	26	445	1.5
B0	60	95	3	4,352	21
B1	87	103	8	1,416	7
B2	75	114	19	622	5
B3	61	114	30	393	3

** Error ± 0.5%

structures and, as a consequence, an effect on the resistance properties is expected. The MEK test was performed to this end. On one hand, all films based on resin A show low weight loss after immersion into MEK and almost no difference is observed between them (without or with additional acrylate monomers). On the other hand, a different behavior is noticed for coatings based on resin B. Film made from formulation B0 is well dissolved into MEK (21 wt%), and this drawback is reduced by the addition of the multifunctional monomers. Due to the long chains and the structure of resin B, formulation B0 leads to the building of low crosslinked film (high M_c). Moreover, it exhibits low conversion—40% of (meth)acrylate groups did not react. Therefore, unpolymerized chains that are trapped within the weakly crosslinked network can be dissolved into MEK. The incorporation of the multifunctional acrylates into resin B leads to the formation of higher resistant samples with lower M_c; and, as a result, there is a lower dissolution into MEK. These results underline high crosslinking and ensure copolymerization between resin B and the acrylate monomers. Even if reactive groups are still remaining, these latter conditions guarantee

efficient trapping and low dissolution into MEK. High resistance to solvent is thus achieved.

Conclusion

To ensure high-resistant UV-powder coatings while ensuring respect of wood-based panels and lowering energy consumption, the reactivity of the original UV-powder systems has been improved—even for a relatively low-temperature curing process—with the addition of multifunctional monomers. Even though some vitrification occurred preventing some cured coatings from reaching full conversion, this phenomenon was shown not to negatively affect the glass transition temperature and the resistance to solvent of the crosslinked coatings. In addition, the differences in properties due to different backbones, length and flexibility of the resin chains were levelled off between polyester methacrylate and urethane acrylate-based coatings when incorporating a multifunctional monomer. Also, the possibility to follow eventual dimensional variations under time and the low temperature process make the studied systems suitable for application on wood-based panels. ▀

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