Towards outperforming and more sustainable vinylic polymers

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Introduction

Life quality nowadays is a crucial issue. Governments around the world are legislating with the purpose of lowering down the emission of pollutants that may affect human health, in particular for those present in closed environments (office, household), affecting the indoor air quality [1]. Taking into account the wall paints application and the production phase of furniture, the use of organic solvents should be avoided, to reduce exposure risks for the operators.
In this scenario, water-based polymer dispersions represent a good option, in particular vinyl-polymers dispersion have a high wettability on surfaces like wood, paper and concrete, a high compatibility with the most used pigments, and are tunable in rheology.
The main drawback of water-based vinyl dispersions is the water and thermal sensitivity, that affect mechanical properties, and generally limit the use of this type of polymers as binder for exterior coatings and as structural adhesives for particleboard, plywood and alike.
To improve water-resistance it is possible to add in the process monomers with high hydrophobicity and hydrolysis resistance such as ethylene and/or vinyl esters of versatic acid, while to improve mechanical resistance, monomers with high glass transition temperature (Tg) like (meth)acrylate acids/esters are useful. And the use of crosslinkable monomers (like N-methylolacrylamide NMA or acetoacetoxyethyl methacrylate AAEMA) or curing additives like dialdehydes improves both mechanical properties and solvent resistance [2]. To perform the polymerization process with monomers having different reactivity ratios requires dedicated feeding strategies, to control morphology and size distribution of the polymer particles.

Wood adhesive dispersions

Urea-formaldehyde (UF) adhesives are the current technology in the production of hardwood plywood, particleboard, and medium density fiberboard. To avoid formaldehyde release soy protein technology could be promising, nevertheless in this type of formulation a crosslinking agent is required (e.g. polyamide amine epichlorohydrin, that is classified as carcinogenic substance). We develop a two-component product based on hydrophobic vinyl-monomers, together with high Tg polyvinyl alcohol, and a crosslink booster. The product meets the CARB NAF requirements (which means that no formaldehyde has been added in the formulation) and the European E-1 Formaldehyde emission standard. UF adhesives release formaldehyde in every step of the production: raw materials, panel production and panel life. The emission of formaldehyde in the other two processes is below 100 ppm or not detectable (according to the EN717-1 test method). In table 1 are reported the main performances of the three technologies. With the vinyl technology, it’s possible to reduce pressing time (saving up to 12%) and temperature, obtaining a panel with even higher mechanical resistance (see table 2). Even the panel converting time (the waiting period between the pressing and the subsequent processing of the panel, during which reactions are allowed to complete) is greatly reduced, because the vinyl dispersion needs only to lose water and the panel is ready to be processed. This behavior could be explained considering the structural difference between a rigid high branched network, constituted by short oligomers bonded together with polyfunctional molecules, and more flexible long polymeric chains with few crosslinking bridges between them (figure 1).

Technology	Raw Material	Resin Type	Application	Pot life	Storage conditions
UF	Oligomers	Thermosetting	Curing (110°C)	Hours	Cool
Soy protein	Oligomers	Thermosetting	Curing (110°C)	Hours	Powder r.t. / catalyst cool
Vinyl polymer	Polymer	Thermoplastic +booster	Room temperature	Up to 5 Days	Room temperature

Table 1. Comparison between different technologies for plywood manufacturing.

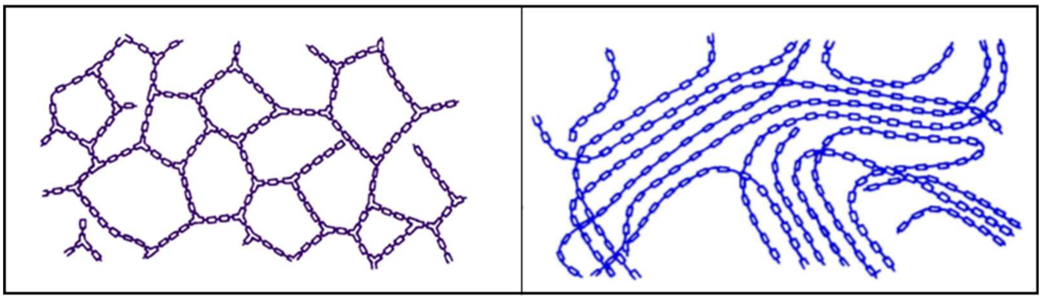

Figure 1. Left: crosslinked network UF. Right: long chains of thermoplastic polymer.

	Vinyl polymer	UF	Soy protein
Curing temperature (°C)	<100	100-110	100-110
Tensile strength EN314-1 (N/mm^2)	1.2-1.7	1-1.5	1-1.5

Table 2. Application conditions and mechanical resistance

Coating dispersion for paints

Vinyl-versatic water-based dispersions are very popular in the paint market as interior coating due to their good rheology and compatibility with pigments and additives, that permit to prepare paint formulations with higher PVC (pigment volume concentration) content and longer open time (slower drying period) than acrylic and styrene-acrylic ones. For a paint application a film formation temperature of 5°C is preferred, but typically the Tg of polymers is higher than room temperature, so quite all paint binders include a certain amount of coalescing agent, to allow film formation at low temperature.

We developed a new generation vinyl-versatic polymer, designed for low-VOC, low-emission, odourless and formaldehyde free paints, to comply the actual ecological regulations (quality standard as French Grenelle Environnement, Italian CAM, German Blauer Engel…). In figure 2 are presented data of wet scrub resistance for 5 samples of interior paint formulations, comparing the new vinyl-versatic product with the standard one, two commercial vinyl-ethylene products and a styrene-acrylic one. Both ISO 11998 and DIN 53778 methos highlight how much better the new product performs in comparison to the standard one with values comparable to those of the styrene-acrylic.

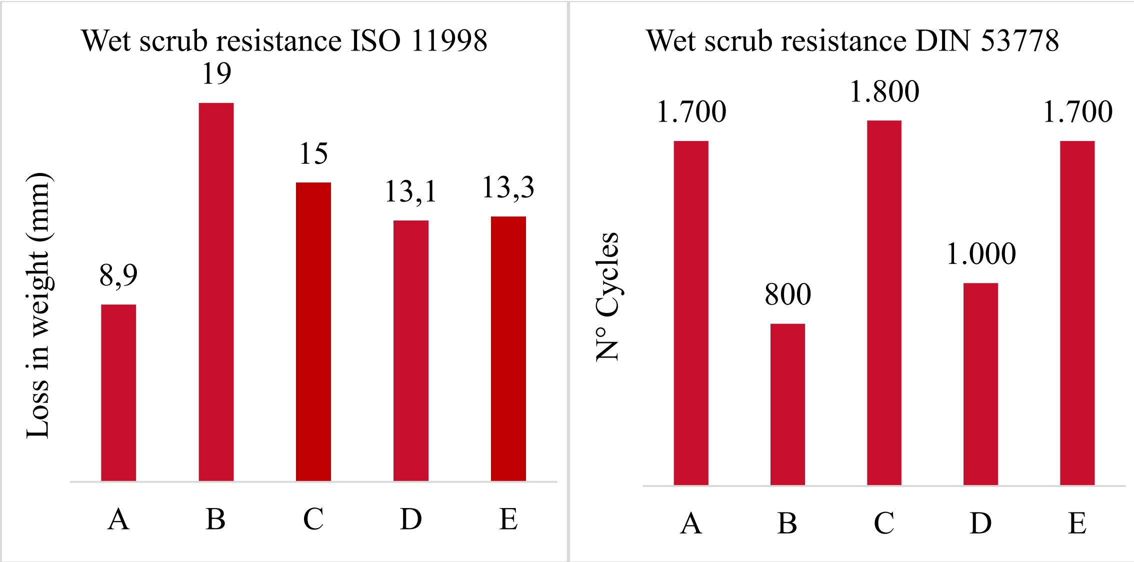

Figure 2. Wet scrub resistance according to ISO 11998 and DIN 53778 methods. A) inonnovative vinyl-versatic, B) standard vinyl-versatic, C) vinyl-ethylene 1, D) vinyl-ethylene 2, E) styrene-acrylic.

In the application as exterior paint, the innovative vinyl-versatic binder shows weathering resistance equivalent to pure acrylic and styrene-acrylic resins (figure 3).

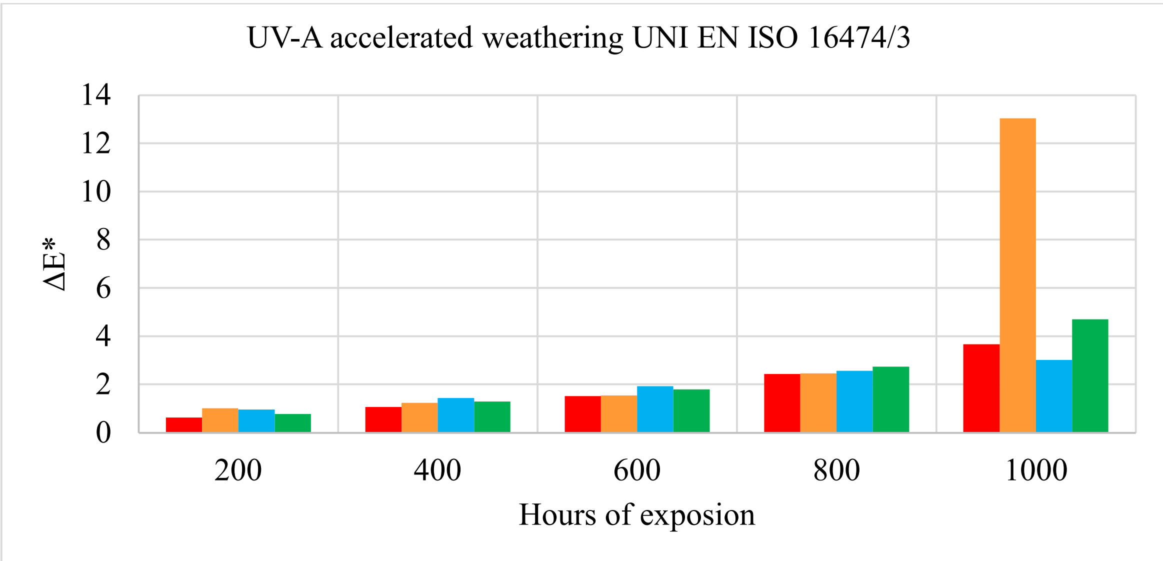

Figure 3. UV-A accelerated weathering of innovative vinyl-versatic (red), standard vinyl versatic (orange), styrene-acrylic (blue) and pure acrylic (green).

Conclusions

With innovative processes and proper formulations, it's possible to improve water-based vinyl dispersions properties, to meet the new ecological regulations and achieve higher performances, fulfilling the market requests. In this work we presented two vinyl-based products suitable for structural wood adhesives and low-VOC binders for interior and exterior paints.

References & Notes

[1] SCHER (2007), Opinion on risk assessment on indoor air quality, 29 May 2007

[2] Open Journal of Polymer Chemistry, 2022, 12, 13-42

EN 314-1:2004 Plywood - Bonding quality - Part 1: Test methods.

EN 717-1:2004 Wood-based panels - Determination of formaldehyde release - Part 1: Formaldehyde emission by the chamber method

ISO 11998:2006 Paints and varnishes - Determination of wet-scrub resistance and cleanability of coatings

DIN 53778-2:1983-08 Emulsion paints for interior use; evaluation of cleanability and of wash and scrub resistance of coatings

EN ISO 16474-3:2021 Paints and varnishes - Methods of exposure to laboratory light sources - Part 3: Fluorescent UV lamps

CARB NAF: California Air Resources Board (CARB) no-added formaldehyde (NAF) certification

ΔE^*: Color distance of the sample from the initial value according to the CIELAB color space