Investigating the Effects of Weathering on Wood Coatings

The aim of this study is to elucidate the effects of weathering on wood coatings for exterior use. By means of analytical techniques as DSC, DMA, tensile test, UV/Vis and FTIR-ATR spectroscopies, it is possible to identify and measure the degree of damage, and so the chemical, physical and mechanical changes caused by degradation phenomena. The results can improve the predictive capability on coatings’ performance (glass transition, elasticity, light transmission) and help the assessment of the protective ability of light-stabilizing additives, in order to satisfy the requirements of coating producers and users.

Keywords: wood, coatings, weathering, UV absorber, HALS

1. INTRODUCTION

It is well known that wood coatings are susceptible to degradation when exposed outdoors in consequence to various weathering, phenomena mainly promoted by light, heat, water and oxygen. The evidence of such negative evolution during a weathering trial is the development of various defects like cracking, flaking and loss of adhesion whose initiation and progress mainly depend on coating formulation [1-6]. This risk is evident, in particular, when advanced manufacturing processes [7-8] or materials are used [9-10].

The lifetime prediction of outdoor exposure on the basis of accelerated weathering data would be of great importance, since the duration of the natural weathering tests is usually much too long to be practical [11-12]. Moreover, the evaluation criteria currently included in the standards EN 927-3 and EN 927-6 (respectively natural and artificial weathering for paints and varnishes for exterior wood coatings) are based on visual assessments of the exposed samples, which are not often exempt from subjective interpretation which lead to a scarce repeatability and reproducibility of the two methods.

In this study various analytical techniques have been investigated in order to identify physical, mechanical and chemical changes in free coating films that indicate the initiation and progress of the degradation phenomena associated to a weathering process. The execution of real measurements of crucial parameters for the coating performance could be extremely helpful not only to improve the reliability and the predictive capability of the above mentioned test methods, but it would also represent a objective and unquestionable support for coating formulators.

2. MATERIALS AND METHODS

The study has been carried out on four clear water-based coating materials (Table 1) expressly formulated and constituted by an aqueous emulsion of an acrylic binder with two different additives: an ultraviolet radiation absorber (UVa) and a hindered amine light stabilizer (HALS). The first additive is composed of an aqueous dispersion of a red shifted 2-hydroxyphenyl-s-triazine, while the second is a dispersion of an aminoether-substituted tetramethyl piperidine derivative. A general overview of emissions related to wood products is available in [13].

Table 1. Composition of the coating materials analysed

| Coating material | Binder | UVa (wt%) | HALS (wt%) |
|------------------|--------|-----------|------------|
| A                | Acrylic| -         | -          |
| B                | Acrylic| 3%        | 1.5%       |
| C                | Acrylic| 3%        | -          |
| D                | Acrylic| -         | 1.5%       |

Each coating material was exposed to artificial weathering in accordance with the European standard EN 927-6 in a proper device, both as coated wood samples and free films (Figure 1).

The coatings were applied by brush to the front and side faces of wood panels (the back was left uncoated) with three coats corresponding to a total spreading rate of (150 ± 30) g/m². After application, the wood specimens were dried for one week in a conditioned room at 23°C and 50% RH.

Free coating films were also prepared using glass plates. The films were applied with a wet film thickness of 250 µm using a bar film applicator. After natural drying for 72 hours in a climatic room at 23°C and 50% RH, the solid films were peeled off from the glass plates by a mild vaporization on a thermostatic bath at (43 ± 1)°C. The dry film thickness was about 100 µm for all samples. Specimens for the artificial weathering were produced by cutting the free coating films in the dimension of 230 x 78 mm and clamping them on specimen holders by a proper sealant.

All the samples were weathered up to six weeks. The degradation effects on wood panels (blistering, flaking, cracking, chalking, loss of adhesion) were estimated by visual assessments according to ISO 4628.
Free coating films were analysed prior to exposure and after two and six weeks of weathering by means of the following analytical techniques: differential scanning calorimetry (DSC), infrared spectroscopy (FTIR-ATR), ultraviolet-visible (UV/Vis) spectroscopy, dynamic-mechanical analysis (DMA) and tensile test. Procedures were compared with similar ones, successfully used in investigating the aging of different materials [14-15].

2.1 Differential Scanning Calorimetry (DSC)

The glass transition temperature (Tg) measured with DSC technique was calculated with the “Half-Cp-extrapolated” method. The analysis was carried out with a temperature scan, from -30°C to +90°C, at a heating rate of 20°C/min, under nitrogen flow. Samples were conveniently prepared by cutting out sections of the film with a standard paper punch, obtaining thin disks of 6 mm diameter; ten or eleven disks (~ 20 mg of material) were collected in the aluminium pan.

2.2 Infrared spectroscopy

Chemical modifications occurring in the binder structure due to weathering were analysed by means of infrared spectroscopy, with the attenuated total reflection (ATR) geometry. The penetration depth of the infrared beam into the specimens is limited to a few micrometres (0.5 ÷ 5 µm) beyond the crystal; so, it was possible to analyse the composition of the outermost superficial layer of the exposed side of the free films. This technique was used to highlight chemical modifications, such as oxidations in the polymer backbones, that occur during the ageing process.

2.3 UV/Vis spectroscopy

Ultraviolet-visible spectroscopy (UV/Vis) allowed to obtain the transmission spectra in the ultraviolet-visible region. Comparisons among the spectra recorded on free films before and after the weathering trials were made, in order to highlight differences among the four coating materials and their possible variations during weathering. The spectra were obtained using a UV-Vis spectrophotometer equipped with an integrating sphere (Ulbricht sphere). The scanning rate was set at 100 nm/min.

2.4 Dynamic-mechanical analysis (DMA)

The viscous-elastic properties of the four coatings were tested by means of a DMA analyser, using a temperature scan test. By applying a dynamic load at low constant frequency while varying temperature, it was possible to detect three parameters which strongly characterize the mechanical response of a polymer [16]: the storage modulus (G′), the loss modulus (G″) and the loss factor (tan δ). The last parameter can be used to determine the glass transition temperature of the polymer Tg. The temperature scanning rate was set at 2°C/min, from -30°C to +50°C. The dynamic stress was axial tensile, with an amplitude of 10 µm. Values of 120 mN and 100 mN were chosen for the static force and the dynamic force respectively, with a fixed frequency of 1 Hz. The dimensions of the specimens were 10 mm x 3 mm; the average thickness was measured with a digital micrometre.

2.5 Tensile test

The mechanical properties of the coating films were analysed by a tensile test in which the sample is fixed between two clamps and subject to an uniaxial tensile force, in accordance with the procedure specified in CEN/TC 139/WG 2 N 858 document. The parameters derived from the stress-strain curve are: the strain at break (εR) and the Young’s Modulus (E). These two parameters play a major role in determining the variation of extensibility of the free films during weathering.

The strain at break is the last recorded data before the stress is reduced to less than or equal to 10% of the strength (if the break occurs prior to yielding). It is correlated to the ability of the polymeric chains to rearrange throughout the stress application and it directly relates to the type of chemical and physical bonds among the polymeric chains and to the bond strength. The less rigid and tightened the chains, the higher the ability of modifying the structure.

The Young’s Modulus represents the ratio between the tensile stress (Pa) and strain (%) in the first part of the stress-strain curve, where it is linear. Graphically, it is the slope of the stress-strain curve in the strain interval between ε = 0.05% and ε = 0.25%.

3. RESULTS AND DISCUSSION

Artificial weathering induces evident changes on the coated wood panels: the surfaces exposed directly to UV radiation and water (spray and condensation) show a noticeable colour change, with a general darkening (Figure 2).
The appearance of degradation effects, like cracking and flaking, induced to stop the weathering trials after only two weeks for formulations A and D, whereas the other two formulations, B and C, endured the weathering for the entire exposure time (six weeks).

The analyses carried out on the free coating films allowed to better understand the causes of such degradation evolutions. During the weathering trials, the coating films underwent chemical and physical changes, different in typology and intensity as a function of their composition.

The DSC measurements highlighted a Tg shift towards higher temperatures. Before weathering (0 weeks), the four coating materials exhibit similar values for the glass transition, that is around 0°C.

During the weathering trials Tg increases. The results reported in Table 2 clearly indicate that the shift of glass transition is a function of the exposure time and the formulation of the coating materials. The polymeric films tend to become stiffer due to the chemical-physical phenomena occurring in the polymeric chains. Coating A, being formulated without photo-stabilising additives, shows a fast and dramatic increase of its glass transition, whereas the other formulations undergo a lower increase depending on the protective action of UVa and HALS additives.

Both stabilizing additives help to limit the increase of the glass transition temperature during the artificial exposure trials, but UVa is more effective: it contributes to a long-term stabilization and has a major role in the retention of the mechanical properties of the coatings during weathering. On the contrary, HALS delays the effects of the weathering process, i.e. it reduces the degradation rate, but it is not able to stabilize the coating films for long periods.

The IR spectra show the typical signals of acrylic binders. The strong peak centred at 1730 cm⁻¹ can be associated to the C=O stretching vibration of ester groups and the bands at 1150 cm⁻¹ are due to the O−C=C stretching vibration, while C−H stretching vibration occurs in the range 3000-2800 cm⁻¹. Figure 3 gives evidence of the changes that occur in the molecular structure of the acrylic binder during weathering.

| Table 2: Glass transition temperature of free coating films assessed by DSC analysis. |
|---------------------------------|--------|--------|--------|--------|
| Tg (°C) | 0 weeks | 1 week | 2 weeks | 6 weeks |
|-------|--------|--------|--------|--------|
| A     | -0.6   | 3.4    | 12.5   | -      |
| B     | -0.2   | -      | 1.3    | 1.6    |
| C     | 0.5    | -      | 2.2    | 2.7    |
| D     | -0.4   | -      | 1.3    | 5.4    |

In particular, the signals associated to an oxidative effect of the resin are: hydroxylation and peroxides formation characterized by a broadening of O-H signal at nearly 3500 cm⁻¹; polymer chain scission connected with decreasing intensities of C-H and C-H2 in the region 3000-2800 cm⁻¹; the increase of aliphatic and...
aromatic carbonyls, with subsequent broadening of C=O signal in the range 1800-1600 cm\(^{-1}\); the formation of carboxylic groups around 1700 cm\(^{-1}\) and C-O bond around 1100 cm\(^{-1}\). The increment of the C−H out-of-plane deformation vibration centred at 1000 cm\(^{-1}\), which corresponds to alkene groups, suggests that also main chain scission occurs during photo-oxidation of clear coats stabilized only with UVa. It was noted that the degradation rate associated with photo-oxidative effects is higher for coatings A and C, whose formulations do not include HALS. In general, the polymeric binder undergoes a much faster photo-oxidation without than with HALS.

This technique was used also to verify the effectiveness of the HALS in combination with the UVa in the prevention of photo-degradation of the binder [18-19], and to analyse their specific photo-stabilization mechanism (Figure 4).

The evidence of the role of UV absorbers is that of protecting the inner layers of the coatings, i.e. in the bulk. Since absorption of ultraviolet radiations and subsequent dissipation in form of heat (red halo around UVa particles in Figure 4) is the physical mechanisms on which is based the UVa effect, it can be expected that coating thickness plays a fundamental role in the global protection of the finish products against sunlight. Then, in coating formulation and use, a particular attention should be paid to the consideration that the final dry film thickness strongly affects the amount of UVa needed.

Another consequence is that the outer layers of the coating films are less protected against light as the amount of UVa is not sufficient to completely prevent their photo-oxidation.

HALS, on the contrary, are more effective on the surface rather than in the bulk. The protection mechanism of HALS, which is not related to ultraviolet absorption but to “quenching” of excited states, according to the Denisov cycle [20], is efficient on the surface layer of the coating films, where it limits the growth of free radicals by trapping them (v-shaped signs in Figure 4) and avoiding the prosecution of the degradation process. Therefore HALS is necessary to inhibit the photo-oxidation on the surface.

Figure 5 shows a comparison of the UV/Vis transmission spectra of the four coating materials studied, prior to weathering exposure (0 weeks). Acrylic films are highly transparent: most of the visible light (400 - 800 nm) penetrates the coating films and in this range the transmission is very high, almost 100%.

The presence of UV absorbers in coatings B and C is easily detectable by a zero or nearly null transmission in the ultraviolet range, below 400 nm. On the contrary, coatings A and D show a gradual decrease of transmission between 480 and 280 nm, and this is a significant evidence that there are no additives able to absorb ultraviolet radiations in these two coating materials.

The role of UVa is to reduce the energy of light penetrating the coating film and reaching the wood-coating interface by absorbing the most energetic (thus harmful) wavelengths. The goal is both to limit the polymer degradation and to reduce the photo-discolouration of lignin [21]. During the weathering trials, the UV absorber is stable and maintains its “shielding effect” throughout the entire duration of the exposure. There is only a weak reduction in proximity of the visible range, since films slightly yellow (Figure 6, up).

The spectra of the coatings containing UV absorbers (B, C) show a very similar trend, whether the HALS is present or not. No changes were observed in the UV transmission spectra of these coatings at different exposure time, regardless the presence of HALS. Therefore their synergism is simply due to their different stabilizing mechanisms.

A further proof of this behaviour arises from the spectra of formulations not containing UV absorbers. They show a dramatic change in the UV range of the spectrum (Figure 6, right), and even though D contains the HALS in its formulation. Therefore HALS does not contribute to UV stabilization of the coating binder.

It can be noted that the modifications in the UV range during weathering (increase of T %) reflect the chemical changes suffered by the binder in consequence to its photo degradation caused by ultraviolet radiations.
Moreover, for the same samples it is also evident the transmittance decline in the visible range, above 400 nm, associated with a loss of transparency or a visual perception of colour change in the coating films due to degradation processes (e.g. yellowing).

Concerning the mechanical properties, it is well known that a coating film must be able to follow the movements of the underlying wooden substrate without losing its adhesion. Therefore, the coating has to keep its full integrity and has to comply these movements, in order to maintain its protective role throughout all its service life. For these reasons the mechanical properties of the free films were investigated by DMA and tensile tests analyses.

DMA analyses confirmed the increase of Tg values with weathering, in particular for formulations A and D that do not contain UV absorbers (Figure 7). The peaks of tan δ curves (which determine the Tg value) clearly shift towards higher temperatures during the weathering trial: for formulation D, the difference between the Tg of non-weathered specimen and the value found after six weeks of weathering is higher than 10°C.

The curves obtained for the viscous-elastic moduli highlighted the sharp increase of the storage modulus G’ in the course of weathering. The behaviour of loss modulus G” is more difficult to explain since it seems less affected by weathering.

A comparison of the efficiency of HALS and UVa in the retention of the mechanical properties of the coating films during the tensile test shows that the simultaneous presence of the light stabilizing additives in the formulation B leads to the best performance (Figure 8).
The variation of the elastic modulus during the weathering trials is strongly dependant on the formulation. In order to perform a protective action, it is required that the film maintains a certain level of elasticity (this depends on glass transition) and that the area under the tensile stress-strain curve is as higher as possible. The area under the $\sigma$-$\varepsilon$ curve is related to the resilience, that is the ability to gain deformation energy before coming to rupture. For this purpose, in terms of protective capability of a coating, the higher the strain at break, the better it is.

Our results show that strain at break decreased during the weathering trial; even in this case, the variation of strain at break is strongly dependent on the formulation and the best performance was found for B. This result gives evidence of the synergetic effect of UVa and HALS: the protective action on a coating is better when they are both present in the formulation.

4. CONCLUSIONS

The main purpose of the study was to identify analytical techniques suitable to assess physical, mechanical and chemical changes in free coating films that indicate the initiation and progression of damages due to weathering phenomena.

Glass transition was studied by means of differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). The results obtained by means of these two different techniques correspond: both give evidence that glass transition temperature shifts to higher values after a coating film is exposed to artificial weathering according to EN 927-6. The greater the variation, the worse the durability of coatings is expected. In particular, DMA allowed to correlate the glass transition temperature with the response to mechanical stress. In consequence of weathering, storage and loss moduli ($G'$, $G''$) increase, since the coating films become more rigid and stiffer. Clearly, the more stable the storage and loss moduli during weathering, the more durable are the coatings.

The investigation also studied the influence of two common additives: an aqueous dispersion of an ultraviolet radiation absorber (UVa), and an aqueous preparation of a hindered amine light stabilizer (HALS).

By infrared spectroscopy (FTIR-ATR) it has been shown that the use of HALS prevents the photo-oxidative phenomena of the outer layers of the coating films. By means of UV/Vis spectroscopy, it has been found that the UVa manages to shield the near ultraviolet range (280-400 nm) very effectively, and its presence is essential to prevent the degradation of the coating films and of the substrate. Coating materials formulated without UVa showed great changes in the ultraviolet range of the transmission spectra, caused by weathering phenomena. The UVa shows a high stability, its absorption efficiency remaining unchanged throughout the entire exposure period (i.e. up to 6 weeks).

The response to mechanical stress was investigated with tensile test. The mechanical properties of coatings vary during weathering: Young’s Modulus increases and strain at break decreases. UVa and HALS play a significant role upon retention of mechanical properties. Apart from the evidence that they behave also as plasticizers, UVa and HALS perform a fundamental synergetic effect on the long-term stability of the mechanical properties of the coating films.

In conclusion, all the techniques used in this study were able to detect and “measure” the degradation of the properties of the coatings during ageing, in particular when UVa is not included in the formulation. Their application is useful for studies upon resins and additives (typology and quantity), and can contribute to improve weathering prediction of wood coatings.

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ИСТРАЖИВАЊЕ ЕФЕКАТА АТМОСФЕРСКИХ АГЕНТА НА ПРЕМАЗЕ ДРВЕТА

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Циљ овог истраживања јесте разјашњење ефеката атмосферских утицаја на лакирано дрво за спољашњу употребу. Помоћу аналитичке технике као што су DSC, DMA, тест на затезање, UV/VIS и FTIR-ATR спектроскопије, могуће је идентификати и мерити степен оштећења, хемијске, физичке и механичке промене изазване деградацијом. Резултати могу да побољшају предвиђену способност перформансе премаза (остакљивање, еластичност, пренос светлости и) и помогу у процени защитне способности светлосно стабилизујућих адитива, како би се задовољило потребе произвођача премаза и корисника.