Photostabilisation of the “wood-clearcoatings” systems with UV absorbers: correlation with their effect on the glass transition temperature.

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Abstract. In an application-oriented study, the effective transition temperature $T_g$ of organic wood-clearcoatings between a hard, glassy state and a viscoelastic and rubbery state is measured. The value of $T_g$ is important in the eventual development of cracks and a thermomechanical analysis is used to study the photostabilisation performance of some UV absorbers. A weathering exposure test suggests that certain organic UV absorbers have quite a low $T_g$ and may inhibit the crack formation, in contrast with inorganic UV absorbers.

1. Introduction and objectives
The lifetime of the wood-clearcoating system is reduced in outdoor service by attacks of solar radiation, heat, moisture, oxygen and atmospheric pollutants. The chemical mechanisms are relatively known [1]: UV radiation can produce photo-oxidation, while high temperature and moisture produce thermal degradation and hydrolysis. Since all these processes change the coating composition, they act against its chemical stability. As a result, the coating toughness decreases and the hygrothermal stresses increase, negatively affecting the coating cohesion and its adhesion with wood substrate. The direct practical results are well known: the detachment and/or cracking of the coating that in turn cause the degradation of wood substrate. Undesirable mechanical, physical and chemical consequences of the resulting degradation can be substantially limited by properly selected photostabilizers such as UV absorbers used in this study. Since organic coatings as amorphous polymers are viscoelastic in nature, the effective glass transition temperature $T_g$, the temperature at which a coating changes from a glassy and hard material to a viscoelastic and rubbery state, is a very important parameter in the wood coating durability. This means that when the film is in the glassy state, the macromolecules or parts of them will not move: the movement is frozen and the film appears hard and brittle. When the film is in the rubbery state, parts of the molecules begin to vibrate. The more energy introduced, the more intense will be the vibration, till the whole molecules move. These molecules in movement need more room and so the film expands and is no longer hard. In this state it becomes elastic like rubber. Then, the $T_g$ value can indicate the film state and then the film flexibility. Since the
wood is a deformable material (swelling and retraction), which can induce stress in the coating film, it is very important to apply coatings with a sufficient flexibility in order to follow without rupture the continual dimensional changes of wood in exterior service. Then, this flexibility can be estimated by the measure of the coating $T_g$ [2].

The aim of this paper is to demonstrate the importance of the UV absorber action on the glass transition temperature during the weathering exposure and its reliability with the “wood-clearcoating” photostabilisation. Understanding such relation is required to improve and predict wood coating durability and especially to help us to know criteria for the development of new powerful inorganic UV stabilizers. This is the objective of our project. In our study, in parallel to the degradation assessment, the $T_g$ has been measured during the weathering exposure. Methods and results are given below.

2. Materials
This research project was performed with a water-borne exterior clearcoating (SC 2321/85) provided by Sayerlack with four different UV stabilizers: an experimental (A) and three commercial products: Hombitec RM 400 (B) as inorganic UV absorber, Tinuvin 1130 (C) and Tinuvin 5151 (D) as organic ones (see table 1). Six different coating systems were prepared from the 4 UV absorbers involved in the water-borne coating SC323/85: 5% A, 1% B, 2% A + 2% D, SC 2321/85 alone, 3% C and 5% D. The combination 2% A + 2% D is of a special interest in order to find photostabilisation synergy between organic and inorganic UV absorbers. The six systems were tested onto two wood species: Grand fir (Abies grandis) and European oak (Quercus) wood. The percentages (v/v) used in this study correspond to the advised proportion to obtain the best photostabilisation performances.

| UV absorber | Experimental | Hombitec RM 400 | Tinuvin 1130 | Tinuvin 5151 |
|-------------|--------------|----------------|--------------|--------------|
| Code        | A            | B              | C            | D            |
| Type        | inorganic    | inorganic      | organic      | organic      |
| Form        | paste        | paste          | liquid       | liquid       |
| Based on    | $CeO_2$      | $TiO_2$        | 2-hydroxy    | phenyl triazole |
| Company     | -            | Sachtleben     | Ciba Chemicals Specialities |

3. Ageing
3.1. Ageing effects
It is a well-known fact that UV radiations, moisture and temperature affect the durability of coatings during weathering exposure. They can not only alter the coating composition through a variety of mechanisms, but they can also generate stresses [2]. A high stress can induce damages such as delamination and/or cracking. This stress is a result of temperature variations (e.g. during heating of a coated wood substrate after UV irradiation or condensation and during cooling after spray), and the difference in thermal expansion coefficients of the coating ($\alpha_T^C$) and the substrate ($\alpha_T^S$). This phenomenon can be simulated to a coating/wood substrate specimen subjected to a periodic normal force resultant $N$ and moment resultant $M$ as illustrated in figure 1 [3]. Periodic variations in the temperature and the deformation of the
wood substrate (shrinkage and swelling) occurring during exterior service can induce important changes in coating like mechanical, thermal or dielectric properties. In practice the importance of these changes lies in the fact that it affects material characteristics such as the elastic modulus $E_F$, the relaxation time and the thermal expansion coefficient. In general the material becomes harder and more brittle. Thermal stress ($S^T$), measured by stress-meter [1], can be written as:

$$S^T = \int_{T}^{T_g} \frac{E_F \cdot \epsilon^T}{1 - \nu_F} dT = \int_{T}^{T_g} \frac{E_F (\alpha^F_T - \alpha^S_T)}{1 - \nu_F} dT \approx \frac{E_F (\alpha^F_T - \alpha^S_T)}{1 - \nu_F} (T_g - T)$$

where $\nu_F$ the Poisson’s ratio of the coating and $\epsilon^T$ is the thermal strain. This equation shows that for an identical difference in temperature $T_g - T$, the higher the values of $E_F$, $\alpha^F_T - \alpha^S_T$ and $\nu_F$, the greater the $S^T$ magnitude will be.

3.2. Experiments

Exposure tests were carried out in a QUV apparatus (from Q-Panel Company). The coated wood panels and finish films were exposed following the artificial weathering test optimized by CTBA (Centre technique du bois et d’ameublement) for wood coatings [4]. The weathering cycle consists of a long initial condensation phase, followed by short intervals of UV-light and water spray (table 2). The results obtained by such artificial weathering test correspond to the ones observed after a natural exposure for a much longer time (10 years for example).

Table 2. Weathering cycle programm.

| Step | Function            | Temperature | Duration | Remarks               |
|------|---------------------|-------------|----------|-----------------------|
| 1    | condensation        | 45 °C       | 24 h     |                       |
| 2    | subcycle step 3+4   |             |          |                       |
| 3    | UV                  | 60 °C       | 2.5 h    | UVA-340nm             |
| 4    | spray               | 0.5 h       |          | 6-7 liters/min, UV light off |
| 5    | go to step 1        |             |          |                       |

Total (1 cycle) 168 h. Repetition of cycle = 4 (i.e. 4 weeks). Total duration exposure = 840 h

The photostabilisation performances of the different systems were evaluated during the weathering exposure from:

- **The degree of cracking** according to international norm ISO 4628/4 [5].
- **The general appearance**: visual scale from zero (no change) to five (severe changes) in comparison to the unexposed reference samples.
3.3. Photodegradation evaluation
Results after 840 hours of weathering exposure for the six tested systems applied on Grand fir and oak wood species are presented in figures 2 and 3.

![Figure 2. General appearance (0: no change, 5: severe changes)](image1)

In terms of general appearance the wood-coating system 1%B, 2%A+2%D, 3%C and 5%D show only small to moderate changes (1 to 2) after 840 hours of weathering exposure. For the cracking degree evaluation, the systems 2%A+2%D, 3%C and 5%D show the smallest changes (∼ 0 degree of cracking). Thus, one can conclude that the general appearance of coating is better preserved and the formation of cracks is reduced especially with the use of organic UV absorbers Tinuvin 1130 and Tinuvin 5151 (systems 3%C and 5%D respectively). Also, the mixture of UV absorbers (2%A+2%D) provide good results.

4. Glass transition vs. ageing exposure
4.1. Definition and methods
Like plastics and glasses, coating films are amorphous macromolecular substances which, when heated, don’t have a defined melting point like metals, but on the contrary, present a softening zone. This zone, which can cover an interval from 10 to 30 °C, is called ‘zone of glass transition’, in reference to the terminology used to describe the fusion of glasses which pass from the rigid to the soft state of the molten glass [6]. Dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC) and thermal mechanical analysis (TMA), techniques that measure mechanical properties, heat flux and deformation, respectively, as a function of temperature under a variety of experimental conditions are among the most used methods to determine the $T_g$. DSC measurements were carried out just to locate approximately the $T_g$ zone and then we used the TMA technique because of its higher sensitivity. Free coating films (thickness 0.15 mm) were heated at 10 °C/min under 0.5 N load tested in tensile mode. Experimental curves as the one shown in the figure 4 were obtained and the onset temperature was assigned to the $T_g$ value. This $T_g$ value corresponds to the mean of 3 measurements at least. Indications of the various types of the coating behavior are given at the top of the plot Elongation = vs. (Temperature) in figure 4. In the glassy state, the strain $\epsilon$ is low and then the material can not be easily deformed. In the transition region, the strain begins to increase and then it is easier to deform the film. At temperatures well above the glass transition in the so called ‘rubbery plateau’ $\epsilon$ is much higher, corresponding to the easiest mobility of polymeric chains in the coating film [7]. In our study for example, the temperature of service (weathering temperature) is 60 °C in irradiation cycle which can decrease in the 0.5 hour spray period. Then, during weather exposure, for coatings having $T_g$ higher than 60 °C are in the glassy state contrarily to the ones having $T_g$ lower than 60 °C which are in the rubbery state. This is very clear with systems based on inorganic UV absorber for which the $T_g$ value exceeds 60 °C and the systems containing organic UV absorbers.
with \( T_g \) lower than 60 \( ^\circ \text{C} \) (figure 6). However, the combination of both organic and inorganic UV absorbers 2\% Experimental+2\% Tinuvin 5151 (2\% A+2\% D) leads to a lower \( T_g \) value but not the lowest since \( T_g \) (2\% A+2\% D)\( \rangle T_g \) (5\%D).

4.2. Influence of the different UV absorbers on the \( T_g \) variations

In general the \( T_g \) of an amorphous polymer (in particular organic coatings) changes according to the structural parameters of the polymer \[7,9\]: the \( T_g \) value increases versus molecular weight, cross-linking degree and the polarity of the constituents and decrease especially versus plasticization. The effective glass transition \( T_{g,\text{eff}}(t) \) variations during the weathering exposure are presented in figures 5 and 6.

In spite of the influence of the degradation process (water leads to plasticization) which can lead to a decrease of the \( T_{g,\text{eff}}(t) \) value, the experimental results show that the \( T_{g,\text{eff}}(t) \) increase at the beginning of the weathering exposure and then stabilizes at an asymptotic \( T_{g,\infty} \) value as shown in figure 5. This increase is due to the reticulation phenomenon which leads to the increase of the linking degree. These variations are typical of a first order exponential decay (eq.
2): 

\[ T_{g,eff}(t) = T_{g\infty} + A_1 \exp(-t/\tau) \]  

with \( A_1 = T_{g,eff}(0) - T_{g\infty} \) and \( \tau \) is a time constant. The next table (table 3) resumes the three equation parameters \( (T_{g\infty}, A_1 \text{ and } \tau) \).

**Table 3.** Model equation parameters.

| System          | \( T_{g\infty} \) (°C) | \( A_1 \) | \( \tau \) (h) |
|-----------------|------------------------|-----------|----------------|
| 5%A             | 79                     | -13       | 82             |
| 1%B             | 80                     | -25       | 90             |
| 2%A+2%D         | 74                     | -16       | 151            |
| SC 2321/85 alone| 79                     | -11       | 111            |
| 3%C             | 57                     | -4        | 136            |
| 5%D             | 62                     | -14       | 112            |

The plot (figure 6) and the table 3 show that inorganic UV absorbers ‘Experimental’ and Hombitec (5%A and 1%B respectively) have the highest \( T_{g\infty} \) values during the weathering exposure time. As we can see from the weathering results, the higher the \( T_{g,eff}(t) \) value (observed with inorganic UV absorbers), the higher the degree of cracking and the worst the general appearance are. There seems to be a strong relationship between the \( T_{g,eff}(t) \) temperature and the readiness to form cracks. This shows a clear relation between the photostabilisation performance and the measured \( T_{g,eff}(t) \) value. In fact, according to the results of the weathering test mentioned above, the systems 3% C and 5% D, which have lower \( T_{g,eff}(t) \) values keep better durability of the coating. As it was shown in literature [8], a coating film with low \( T_{g,eff}(t) \) can better fit the dimensional variation of wood.

5. Conclusion and perspectives

It was demonstrated in this study that UV absorbers can improve the durability of the wood-clearcoating systems by inhibiting the cracks formation. The measurement of the glass transition temperature following the weathering exposure shows that organic UV absorbers (C and D systems) which have lower \( T_{g,eff}(t) \), prevent the crack formation compared to inorganic UV absorbers.

This important relation can hinder the future development of new inorganic UV absorbers for exterior wood clearcoatings. As a matter of fact, these absorbers increase the coating \( T_{g,eff}(t) \) value after weathering exposure in spite of their excellent UV protection in interior clearcoating service [9].

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