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DMA analysis to predict the performance of waterborne coatings

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Abstract In previous studies some waterborne coatings, specifically formulated for the scope of the research, were studied during an artificial weathering process by means of dynamic mechanical analysis (DMA) technique. In those studies the chemical and physical parameters which mainly affect the performance of coatings and their evolution during weathering were measured. The aim was to predict the performance of coatings for exterior wood during their service life by means of accelerated artificial tests and instrumental measures. In this study four commercial products were artificially weathered following the European standard EN 927-6. The changes in the mechanical properties were measured by means of the DMA as reported in the previous studies. With this research the authors have verified the capability of this method to predict the performance in use of coatings.

Keywords Wood · Waterborne coatings · DMA · Weathering

Introduction

Wood is an important material employed in a broad range of applications such as building, construction or furniture, due to its versatile properties [1–3]. However, being an organic material, some inherent drawbacks exist. In particular, when exposed outdoor, a complex interaction with chemical and physical factors contributes to what is described as weathering.

Wood is a blend of three organic polymers [3–5]: cellulose, hemicellulose, and lignin. In particular lignin has chromophore-rich groups with high molar absorption coefficients in the UV region. This leads to the formation of free radicals [6–8] when wood is exposed outdoors which cause degradation of lignin and photo-oxidation of cellulose and hemicellulose. Other factors contribute to wood degradation such as moisture, rain, temperature variation, insects, and pollutants [5, 6, 9–12].

One way to protect wood from dangerous atmospheric agents is the application of organic coatings which are able to act like a shield between the external environment and wood. However, being organic polymers, coatings are themselves subjected to weathering. Coating degradation is due to complex chemical-physical phenomena as a consequence of the interaction with environmental factors [4, 9, 13, 14].

In particular, the chemical modifications of coating materials in outdoor applications are caused by the UV region of the spectrum of the solar radiation [6, 7] which promotes a complex series of photochemical reactions.

The effects of weathering lead to important changes in the material at molecular level (oxidations, radical formation, change in polymer structure, change in molecular weight distribution). These chemical modifications can be detected at a macroscopic level as: change of colour, change of gloss, cracking, chalking, etc.

In addition to these chemical changes also some physical phenomena can occur as an increased molecular packaging and solvent loosing (whit a consequent volume reduction and internal stress formation) which contribute to the degradation process: the final effect of coating

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degradation is the loss of protective performance toward the substrate.

The aging problems of coatings drive the research to follow two main directions:

i.) development of new formulations more resistant to weathering;
ii.) set up of new test methods to predict the coating durability.

As far as the first issue is concerned, coating formulators use different strategies in order to guarantee a long durability of the coatings, considering different resin types, UV absorbers, radical scavengers and different types of pigments.

The development of an adequate test method is quite complex and many efforts are made in this field by researcher, as well by standardization committee [15, 16]. In this area the researchers should realize two goals:

1. setting up fast and reliable test procedure;
2. simulate the stress levels of the material such as in use conditions.

Nowadays, wood coatings for exterior use are mostly tested following the European standard EN 927-3 based on a natural weathering test. However, this method presents two major drawbacks. The first concerns the fact that 1 year is required for the completion of a natural weathering test, which is in conflict with the requirements of the manufacturers who need a rapid evaluation of a new coating. Sometimes an even longer period of time is required, especially when different products are being compared. The second limitation is due to the evaluation criteria, which are based on visual assessments of the exposed samples, not on physical measurements of parameters characterizing coating degradation. At the end of the trial, the panels are evaluated for a range of parameters according to different standards:

- Change of gloss ISO 2813
- Change of colour ISO 7724
- Chalking ISO 4628-6
- Blistering ISO 4628-2
- Flaking ISO 4628-5
- Cracking ISO 4628-4
- Adhesion ISO 2409

According to each of the standards mentioned above, the coatings receive a *score* which is used to evaluate the performance and the conformity of wood coatings.

Another way to test a coating relies on lab-based test methods where adequate devices are employed. In this case an accelerated artificial weathering is carried out under controlled conditions of UV irradiance, temperature, and relative humidity with the optional possibility to simulate environmental condition through cycles of spray and condensation. Such kind of test is relatively fast (for instance for European standard EN 927 the artificial trial takes 2016 h instead 1 year for the natural one) and allows to monitor coatings weathering under reproducible conditions, but presents the same limitation due to the subjective evaluation criteria.

In this study the authors present the results on the use of rapid weathering methods and their evaluation by laboratory measuring techniques, which substitute simple visual assessments.

This procedure, partially developed in previous studies [17, 18], where non commercial products were used, was adopted in order to check coating variations at molecular level during weathering trials: in principle, chemical and structural variations (e.g., mechanical and spectroscopic properties) could be directly related to coating durability.

Coating films normally used for wood protection are thermoplastic organic polymers with viscous-elastic properties. Consequently their mechanical behavior is similar both to solid materials (elastic properties) and to liquid substances (viscous properties). This complex mechanical behavior can be deeply studied by using DMA [19–22].

The data obtained from DMA [17, 18] showed that the absolute value of T_g is not related with the coating durability evaluated following the EN 927-6 standard. The contrary occurs for the evolution of T_g during the weathering test. The formulation which showed a lower augment of their T_g has a higher durability.

In use, due to variations of temperature and humidity, wood is subjected to dimensional changes which induce stress at the interface with coating. That means that an important feature for a coating is also its capability to follow the movements of wood in order to avoid the formations of high stresses at interface that could lead to a detachment of the coating itself.

Experimental procedure

Materials and sample preparation

Four commercial waterborne coatings for wood for exterior use, supplied by the same manufacturer, were studied. Being commercial products, their behavior in use is well known and the classification, in terms of durability, is reported in Table 1.

The preparation procedure is the same employed in the previous studies [17, 18]. The films were prepared in the laboratories of CATAS (San Giovanni al Natisone, Udine, Italy): the varnish was spread on glass by means of film-spreader set to obtain a wet film thickness of 250 μm. When dried, films were detached from substrates by mean

Table 1 Products and their durability

Product	Durability
G	Very high
H	High
I	Sufficient
L	Good

of water steam at 40 °C and conditioned for a week in the same chamber at 20 ± 2 °C and 65 ± 5% relative humidity (RH).

Weathering

The weathering trial was carried out in a Q-UV system which allows to set the environmental conditions (temperature and irradiation) and their duration.

In this study the cycle applied is described by EN 927-6 standard. The cycle consists in a weekly cycle (168 h) composed of UV-A ray exposure, condensation and spray phase, repeated 12 times for a comprehensive duration of 2016 h. The samples were analysed at 0, 1008, and 2016 h.

The films were fitted in the sample holders without a stand on the back, in order to avoid possible breakages.

DMA

The mechanical properties of viscous-elastic materials like polymers are tested by means of a Perkin Elmer DMA7 analyser, using a temperature scan test.

By means of this technique the authors can obtain three parameters which characterize a polymer: the storage modulus (E'), the loss modulus (E''), and the loss factor (usually known as tan δ).

The loss factor can be calculated as the ratio of the loss versus the storage modulus [22, 23]:

$$\tan\delta = \frac{E''}{E'}$$

The tan δ can be interpreted as an index of the visco–elasticity of the material, being defined as the ratio between the viscous component and the elastic component of material. So a material with high value of tan δ (high E'', low E') has a more viscous behavior as one with lower value of the tan δ (low E'', high E').

In a typical thermogram of a polymer the tan δ curve has one, or more, peak commonly assumed to be the glass transition temperature (T_g) of the material.

The temperature scan test was chosen with a fixed frequency of 1 Hz. The pulling stress was axial tensile with amplitude of 10 µm. The dimensions of cut samples were 10 × 3 mm; as thickness was assumed the average value of four measures, obtained with a digital micrometer, on films. Each sample was tested three times.

Results and discussion

The weathering process adopted is quite hard for the free varnish/coating films: products of poor quality are not able to stand the test, as happened to sample I. During weathering coating becomes progressively more brittle and unable to resist to the stresses due to the spray phase: sample I, after the first 1008 h of weathering, was so fragile that DMA measurements were impossible and this explain the absence of the data at 2016 h in Fig. 1, where T_g values versus time of weathering are reported, and in Table 2.

Figure 1 clearly shows that T_g increases during weathering and, more important, that the higher is the quality, the lower the increase.

To predict the durability of a coating when applied on wood also mechanical properties play an important role. In use, due to variations of temperature and humidity, wood is subjected to dimensional changes which induce stress at

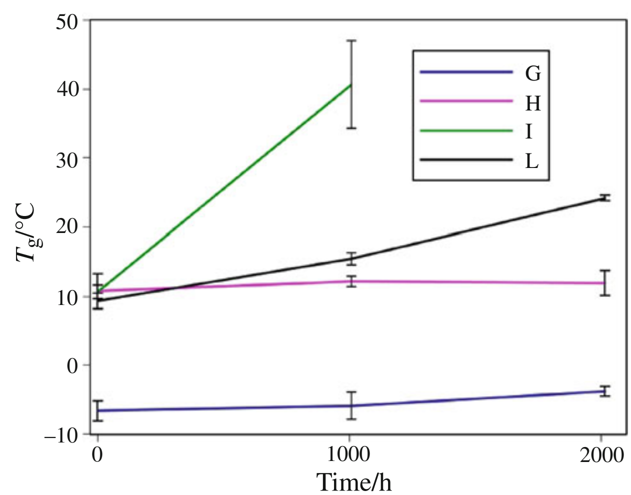

Fig. 1 T_g variation during weathering trial

Table 2 Visco–elastic parameters before and after the weathering

Sample	E'/MPa	E''/MPa	tan δ
G	354	91	0.269
	486	96	0.198
H	206	55	0.267
	237	66	0.279
I	93	23	0.250
	–	–	–
L	235	60	0.253
	415	106	0.253

the interface with coating. That means that an important feature for a coating is its capability to follow the movements of wood in order to avoid the formations of high stresses at interface that could lead to a detachment of the coating itself.

The data, reported in Table 2, show that the H sample has a good combination of visco–elastic properties: a low value of the E' modulus and a high value of tan δ. This means that inter-facial stress, due to wood deformation, will be low and easy relaxed by viscous movements of coating.

As mentioned before, coatings are complex systems composed by a number of products added to give particular features or to modify some behaviors of coatings. So, the resistance to weathering of a coating is not only dependent on the chemical composition of binder but also on the amount and quality of the additives. For this reason it is impossible relate the data collected by means of DMA only with the chemical composition of binder: anyway, the systematic application of DMA investigation, extended in this study to commercial products, confirms that data obtained with this technique are good indicators of quality coating.

It should be underlined that, when transparent films are studied, the situation is also more difficult due to the degradation suffered by the underlying wood by UV radiation which reaches the wood. So, in order to give a complete set of data capable to predict the coating performance, the useful indication obtained by DMA should be improved by additional analysis, such as those reported for the previous set of coatings (tensile test, IR, and UV-Vis measurements).

The whole of these results will finally offer the producers the potential not only of verifying the coating performance with reliable test methods but also of improving their products by systematic variation of formulations.

Conclusions

Four commercial waterborne coatings for wood for exterior use were studied, during an artificial weathering trial, by means of DMA.

It has been confirmed that a correlation exists between the stability of the T_g and the resistance to weathering of coatings as well as with their mechanical properties (such as the E' and E'' modulus and their ratio, tan δ), as preliminary tested in previous studies [17, 18].

The proposed approach provides a fast weathering time under reliable test conditions and is also able to provide important information on the behavior of coatings during an aging test and to predict the durability of coatings during their service life. The DMA, supported by other analysis, can give also important information to producers in order to improve their product.

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