

Bio-based additives for sun protection factors in coatings

Brecht Demedts | Myriam Vanneste | Elke Van De Walle

Sun protection factors have received a lot of attention recently. The growing awareness of health problems has led to increased attention to the use of sunscreen and a greater demand for clothing that protects children and adults from harmful UV light from the sun.

This is because the sun radiates very broadly in the electromagnetic spectrum. Most of this radiation does not reach Earth's surface, as we are well protected by our planet's magnetic field and a thick atmosphere with an efficiently blocking ozone layer. However, in addition to visible light, there is a fraction of highly energetic UV light that reaches Earth, especially UV-A (315-400nm) and UV-B (280-315nm) radiation. UV-B in particular is highly energetic and is known to be a major cause of skin cancer. And while this cancer can be easily detected with a regular visit to the dermatologist, it is a notoriously deadly cancer if detected too late and causes metastases.

In fact, not only humans suffer from the mutagenic effects of sun rays on our DNA, but the same goes for all other life on our planet. Therefore, nature adapts by creating a range of natural UV protectants. There are several ways to protect biological life from UV rays. In a first way, UV light is prevented from reaching the underlying layers. This is done efficiently by pigments or particles that are impermeable to UV (e.g. dark tannins in seeds). Well-known "synthetic" examples in this regard are titanium dioxide and zinc oxide, white pigments that are also used in sunscreens with a high protection factor. The second method of UV protection is the use of so-called UV absorbers. These are molecules that absorb high-energy UV rays and emit them as lower-energy blue light in a process better known as fluorescence.

Many such natural compounds exist, whose function is to attract pollinators such as bees (who see flowers much more spectacularly than humans) or to serve as efficient UV protection molecules in seeds, leaves and fruits. In this study, we wanted to look at the effect of such natural molecules on UPF factors when incorporated into coatings. To work responsibly, we selected natural (colourless) additives exclusively from waste streams. The selected molecules were resveratrol from grape skins, hesperidin and neohesperidin as a type of flavonoids found in orange peels and a very pale coloured tannin extracted from pale seeds (flocan, Ajinomoto). Besides the natural additives, a benzoyl plasticiser (benzoflex, Eastman) and two commercial UV protectants (hostavin 3326, Clariant and tinuvin 400, BASF) were also tested (Figure 1).

Besides blocking or neutralising UV radiation, antioxidants can also be used to reduce UV-induced damage, but this was not included in this study.

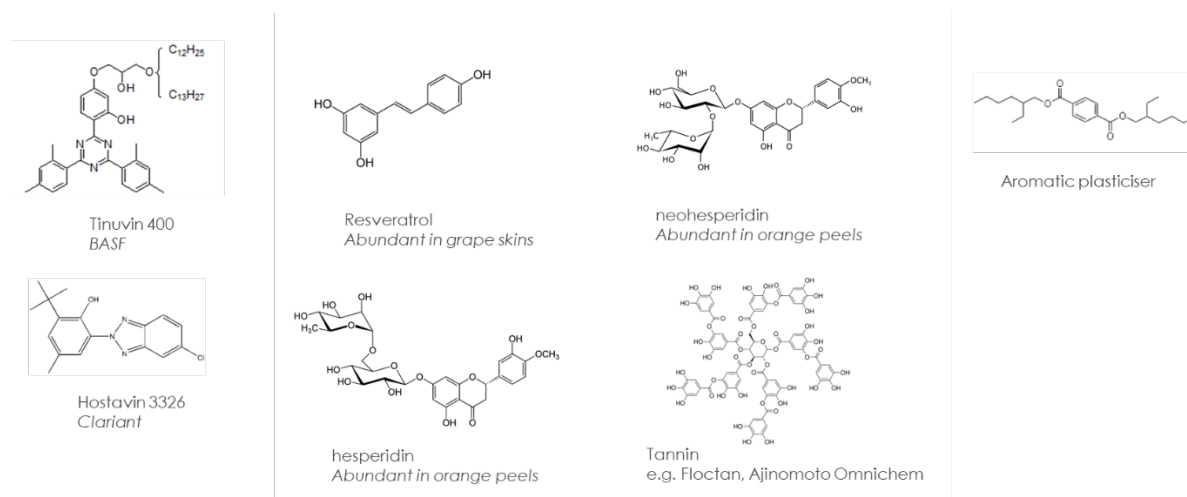


Figure 1: a selection of commercial UV absorbers (tinuvin 400 and hostavin 3326), four natural UV absorbers from waste streams (resveratrol, hesperidin, neohesperidin and tannin), and as a negative control an aromatic plasticizer (benzoflex) were taken in the study.

All additives were added to a commercial PU dispersion (Edolan CM, Tanatex) at a concentration of 1.3, 2.6 and 4.2%. A UV protection factor was measured using the Solar Light SPF-290AS UV transmission instrument. In fact, a UPF factor is an average calculated over the values of UV light transmission between 290 and 400nm. It gives an idea of how well a coating or sunscreen protects the skin, but there are some common misconceptions. For example, there is no linear correlation: an SPF of 30 is not "twice as good" as an SPF of 15.

In fact, it is more of a measure of the degree of protection. In fact, it is more of a measure of what proportion of the sun's rays are blocked. For example, SPF2 means that $\frac{1}{2}$ (or 50%) of the sun's rays are blocked, while an SPF15 only lets through 1/15 of the sun's rays (>93% are blocked) and SPF50 only lets through 1/50 of the sun's rays (98% are blocked). While this is a descriptive measure, there is no correlation with how much sunburn you will get, as it depends heavily on skin type, location, time of day, season or duration of sun exposure. As expected, the UPF factors of commercially developed UV absorbers were much higher than those of biobased molecules. While commercial UV absorbers provide protection of UPF 100 or higher, the best biobased additive achieved a UPF of 80 (Figure 2).

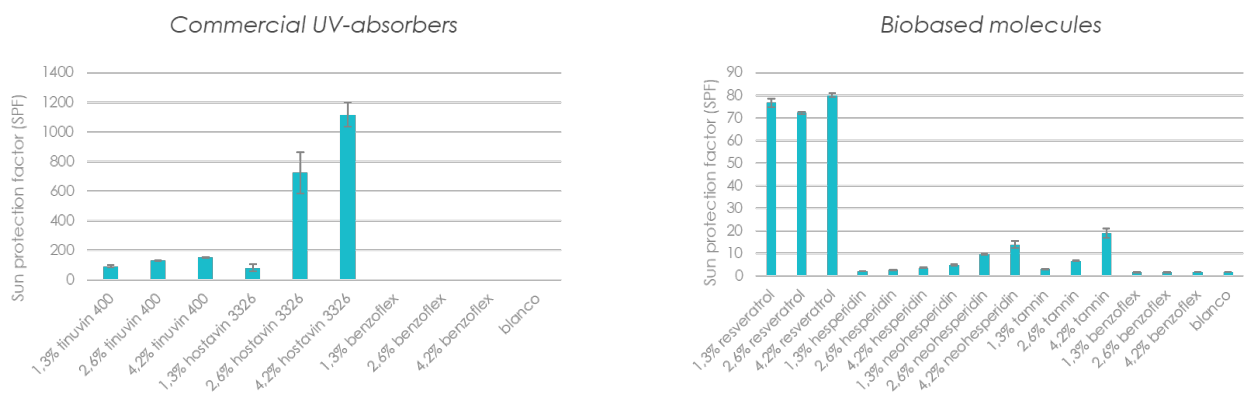


Figure 2: UPF factors of commercial UV-absorbers (left) and biobased molecules (right) when used in concentrations of 1.3, 2.6 and 4.2% in thin film coatings of 50µm thick.

It should be noted that resveratrol is already very active at low concentrations. However, due to the way the UPF factors are calculated, it will never reach a UPF factor higher than 80. The reason for this is illustrated in Figure 3, which shows that commercial blockers such as hostavin 3326 or tinuvin 400 block UV light quite efficiently across the entire UV spectrum (without permeability in neither UV-A nor UV-B), while in the case of resveratrol we see excellent blocking of UV-B but only partial blocking of UV-A. This suggests that bio-based molecules can still be useful when combined. For example, if resveratrol were combined with a blocker that is highly efficient in the UV-A region, such a mixture would offer much higher UPF factors.

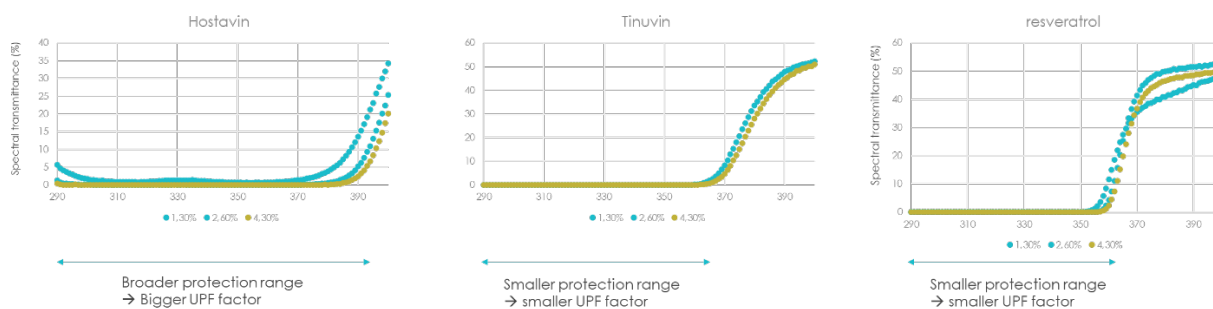


Figure 3 - in order to achieve high UPF factors, spectral transmittance must be good across the whole range of UV-A and UV-B (290-390nm). Components such as resveratrol show an excellent blocking of spectral transmittance from 290-350nm (UV-B range), but higher wavelengths are not blocked efficiently by resveratrol.

In summary, this study shows that UV protection can be achieved by applying very thin coatings with low concentrations of transparent UV absorbers. It further shows that measuring UV transmission can help formulate and evaluate compounds, such as the biobased additives in this study. This study also shows that the activities of the flavonoids and tannins tested are moderate, but resveratrol has very good UV-B absorbing activity.

For more information on UPF testing, feel free to contact Elke Van De Walle, manager of the physical lab at Centexbel.