Influence of initial season on PVC weathering

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ABSTRACT

The forecast of the aging behavior of PVC items from the initial stage of formulation design is crucial and relies on accelerated weathering devices. However, running outdoor weathering tests is necessary to achieve more realistic data. Natural aging norms do not specify the initial season of exposure as a parameter, but there are natural outdoor exposure studies outlining the importance of this aspect and indicating that the lowest degradation is obtained when exposure program starts in autumn and the highest one is observed when exposure starts in winter. Therefore, the first aim of this work is to understand if the initial exposure season affects the final results. Another aim, is the investigation of the effect of titanium dioxide loading to understand if the increase in cost formulation, is worth the stabilization effect. The last goal, is the understanding of the effect of stabilizers' types: tin-based ones mostly used in North America, compared to Calcium Organic ones mostly utilized in Europe. As for the first aim, neither the graphical comparison of discoloration data, nor their statistical analysis confirmed that starting season has a significant effect on degradation. As for the second aim, the same analysis showed that the increase of titanium dioxide from 7 to 9 phr (parts per 100 parts of PVC) is irrelevant on degradation rate. As for the effect of stabilizer type, our analysis indicated that there is a significant difference among only one tin-based stabilizer compared to the others.

1. Introduction

Accelerated weathering test [1–8] are commonly used to test plastic articles durability, but natural outdoor one, although longer, are closer to reality. Very few studies have been published to investigate also the effects of different natural and artificial aging parameters, as temperature [9], radiation sources and water spray [10], geographical areas as Arizona, Ohio, and Florida [11], but the effect of starting season of exposure was not studied. EN 13245-1 [12], EN 877-1 [13] and EN 877-2 [14] establish a system to determine the natural weathering resistance of unplasticized PVC profiles intended to be used for building application describing appropriate values of many parameters, but initial starting season. A study by B. Cora [15] indicated that "the lowest total color difference is obtained when exposure program starts in autumn and the highest total color difference is observed when exposure starts in winter", thus suggesting the importance of this parameter. In particular, that study was based on a 5-years exposure outdoor, in South of France, of series of white profiles stabilized with Calcium Organic Stabilizers (COS), whose color fastness was measured every 6 months in

terms of Delta E. In this work, two organotin stabilizers and three COS were tested, each at 7 and 9 phr (parts per 100 parts of PVC) titanium dioxide concentration. Each sample was exposed five times, starting in four different seasons and the same season for two consecutive years for 4 years. That is done to have a precise idea of the significance of the starting season on discoloration. The discoloration of all samples is fully compliant with EN 12608-1 norm on "PVC-U profiles for the fabrication of windows and doors" under accelerated weathering with Xenotest according to EN 513, severe climate set-up (i. e. Delta E and Delta b* were lower than 5 and 3 respectively).

Thermal and photochemical phenomena act simultaneously during the natural weathering of PVC. It is well known that PVC degrades thermally through a concerted zip-like elimination of HCl with consequent conjugated double bond formation. Studies [16–18] have confirmed that free radicals promote zip-like elimination by ion pair mechanism. These are consistent with a zip-like elimination catalyzed (also) by HCl [19].

Although some thermal and photodegradation mechanisms features are the same, photodegradation has specific peculiarities that lead to a

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cyclic oscillation of the color of the samples during aging. The Theory section (§ 2.) outlines the chemical mechanism underlying this peculiar behavior and to have a comprehensive picture of the photodegradation phenomena.

A first aim of the study is the comparison of outdoor aging started in different seasons to verify Cora's statement, using graphical evaluations and a statistical tool too.

A second aim is the evaluation of the effect of the titanium dioxide loading increase. Titanium dioxide acts as a protective, but expensive pigment and its increased loading should be justified only if it brings a significative better article lifespan.

In addition, many stabilizer types are available on the market and, in particular, tin-based ones are mostly used in North America, while COS are mostly used in Europe. Thus, the identification of significant difference between these types of stabilizers is a third goal of this study.

2. Theory

2.1. Photodegradation and photooxidation

Fig. 1 outlines the overall first stage of the mechanism of PVC photodegradation in the presence and absence of oxygen (full lines in Fig. 1). In absence of oxygen, polyene sequences formation occurs as well as crosslinking and chain scission. In presence of oxygen, chain scission occurs mainly [20].

The calculated quantum yields proves that the presence of oxygen enhances chain scission beside triggering the generation of peroxides and ketones.

Then, the reaction goes further in a second stage (dashed lines in Fig. 1), leading to photocleavage of peroxides and ketones and generating further initiating radicals.

In the third stage, the UV screen from the generated polyenes protects the matrix from further degradation.

As PVC is transparent at wavelength <250 nm, it is thus reasonable that the initiation is due to impurities-chromophores. Polyenes, hydroperoxides, and ketones are the possible chromophores, but due to their high extinction coefficient, polyenes rapidly become the main absorbing chromophores [20]. In particular, as sunlight is screened by the atmosphere, and only wavelengths longer than 290 nm can reach the ground, only polyenes sequences with more than four double bonds can interact with sunlight [21].

Moreover, photodegradation studies in the presence and absence of oxygen showed the independence of the quantum yield of hydrogen

chloride (HCl) on the irradiation time and the initial amount of unsaturation. That leads to the hypothesis of alkene-photo-sensitized degradation processes [20,22].

The same initiation occurs in O_2 and its absence, as the excited singlet polyenes (with very short lifetimes; about 10^{-9} s) cannot be quenched by O_2 [20].

Beside (photo)oxidation, bleaching also occurs due to oxygen presence, leading to shorter polyene sequences both in absence and in presence of irradiation [23].

2.2. Segmentation of degradation layers

Studies on the generation of polyenes and carbonyl species in the presence of stabilizers have been done and led to the conclusion that the (photo)oxidation is diffusion controlled [24]. This concept was completed by further studies on crosslink/chain scission ratio, molecular weight, presence of polyenes and carbonyl species along the thickness of an article exposed to sunlight [25].

That showed that there are three zones (roughly indicated by the different colors in Fig. 2 [26]) along the thickness of a PVC article exposed to sunlight:

1. A superficial one (about 50 μm thick) with the predominance of oxidation products and chain scission. In this region, oxidation is O_2 diffusion controlled, and chain scission results from oxidation reactions
2. A lower zone (between 50 and 300 μm) with a predominance of conjugated polyenes. This region is dominated by crosslinking (resulting from C• radicals) and polyene growth
3. An undegraded core zone beyond 300 μm. In this region, photochemical reactions do not occur as the photons are screened by polyenes when they are more and more generated after a specific time.

The formation of the two superficial degraded layers is in accordance with the following steps:

1. At the beginning of the exposure, the irradiation layer is thicker than the diffusion-controlled oxidation-layer
2. Later on, polyene build-up provides a screen effect, and the irradiation layer become thinner than the oxidation layer: this prevents any progression of the oxidation front towards the core
3. At a certain point in time, the superficial layer is embrittled by oxidative chain scission and cracks
4. The polyenes, lacking their « protective layer», undergo photobleaching, shifting the boundary between degraded zones towards the core. That is why the color of the sample changes during weathering (Fig. 3).
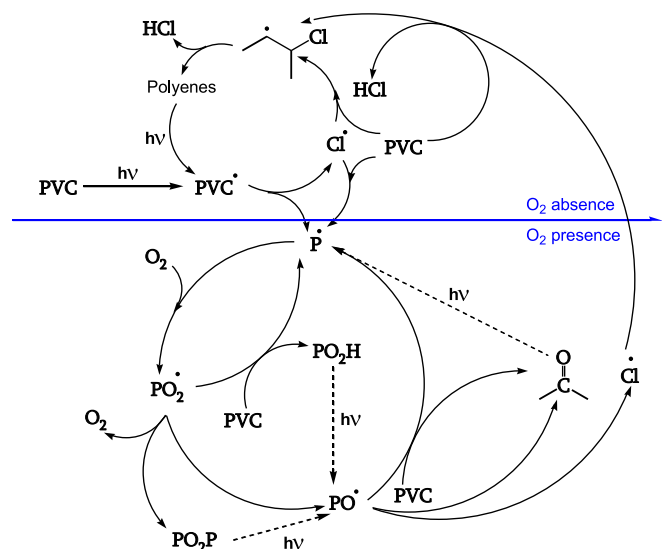

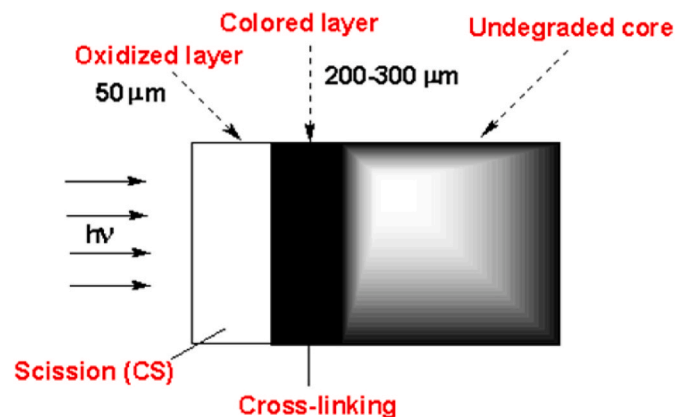**Fig. 1.** Overall photodegradation of PVC (—— first stage; – – – second stage).

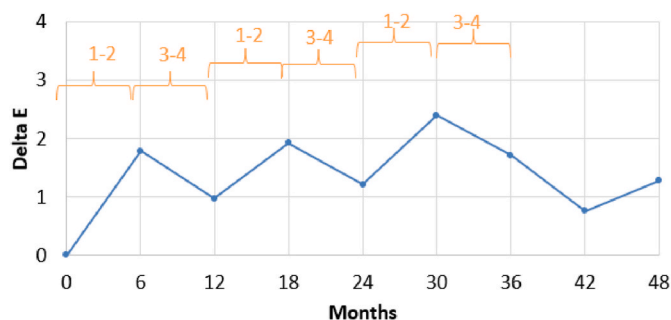**Fig. 2.** Segmentation of degradation layer.

Fig. 3. Color change of a PVC article exposed outdoor (numbers are correlated with the steps above). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

2.3. Effects of pigments and fillers

2.3.1. Effects of pigments

In pigmented articles (e. g. with titanium dioxide), the light penetration depth is lower than in unpigmented articles. The ratio of light penetration depth unpigmented/pigmented is ~5. However, the thickness of the degraded layer is ~3 [27].

That is due to the following reasons:

1. UV light penetration decreases with time as polyenes build-up
2. Small radicals OH● and Cl● diffuse beyond irradiation layer
3. Photoreactions can be initiated by wavelength radiation close to the TiO$_2$ cut-off.

In addition to its screening effect, TiO$_2$ (in particular if not adequately coated or in the Anatase form) is also well known to promote polymer degradation [28].

2.3.2. Effects of fillers

Fillers influence the degradation and chalking of weathered PVC articles as well. For example, one of the most widely used ones, calcium carbonate) worsen the weathering [29], likely due to its reaction with hydrogen chloride, generated by PVC degradation, giving the water-soluble calcium chloride.

2.4. HCl effect on carbonyl formation and inhibition

Although in the photooxidation scheme the role of HCl seems limited to the part of PVC where oxygen is absent (Fig. 1), nevertheless, it still seems to play a role in the carbonyl formation and inhibition. This consideration stems out from the observation that there is a first auto-catalytic phase in the formation and a subsequent inhibition phase for carbonyl species [30]. The initial auto-acceleration and the final auto-inhibition (Fig. 4) are both favored when the thickness is high: their kinetic behavior seems thus controlled by the diffusion of a reactant from the sample to the atmosphere.

HCl (a gas) may fit the description of this reactant. The phenomenon was explained with the initial auto-acceleration catalyzed by HCl, with hydroxyl radical formation (Fig. 5).

The final auto-inhibition catalyzed by HCl, was explained by the formation a charge transfer complex with polyenes (Fig. 6), which is not photochemically active (differently from polyenes themselves).

3. Experimental

As the evolution of conjugated double bonds during degradation directly correlates to color change, degradation is evaluated according to variation of the color of the samples. When a color is expressed in CIELAB spherical color scale, L* indicates lightness, a* indicates the red/green value and b* the yellow/blue value. A color movement in the +a
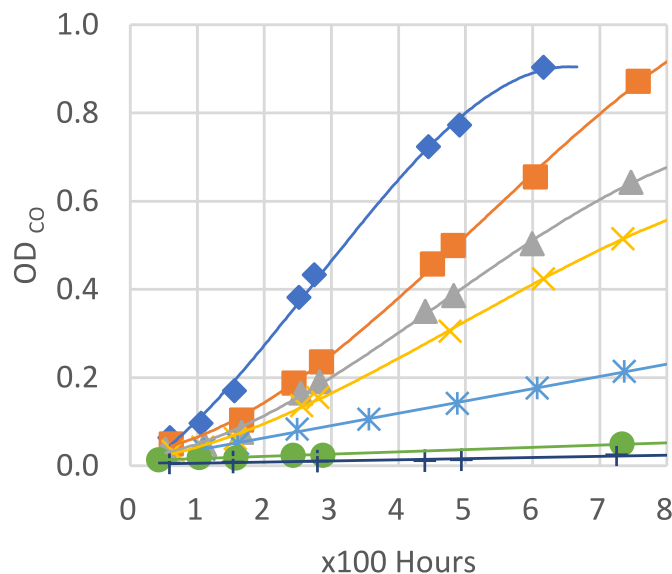

Fig. 4. Optical density of carbonyl peak vs. exposure times for films at a different thickness (from 16 - green dots - to 175 μm – blue diamonds -). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)
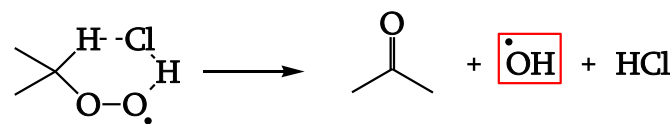

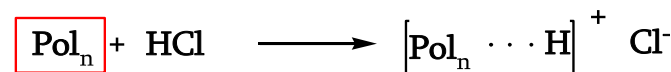**Fig. 5.** HCl-catalyzed hydroperoxide decomposition.

Fig. 6. HCl inhibition of polyene reactivity.

direction represents a shift toward red, while in the +b direction represents a shift toward yellow. The center L* axis (with a* = 0 and b* = 0) denotes total black, while L = 100 denotes total white. The expressions for these color differences are Delta L*, Delta a*, Delta b* (or DL* Da* Db*), (Delta or D symbols indicate difference). Delta E (or DE) = [(DL^2) + (Da^2) + (Db^2)]$^{1/2}$. As DL*, Da*, Db* can be either positive or negative it is preferred to express color difference as their absolute values (to remove any negative sign in front of a number, and to see of all numbers as positive): |DL*|, |Da*|, |Db*| symbols are used to indicate this. Evaluations were based on Delta E, this being the most representative of the overall color change, but similar evaluations may be done on L*, a*, b* evolutions.

As for statistical evaluations of significance of differences, p-value is taken as reference.[1]

Exposure of the same samples was carried out five times:

- Starting in Summer 2013

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[1] The P value is defined as the probability under the assumption of no difference (i. e. null hypothesis), of obtaining a result equal to or more extreme than what was actually observed. The P value measures how likely it is that any observed difference between groups is due to chance (e.g. P = 0,01 means a statistical significance at 1%). Values close to 0 indicate that the observed difference is unlikely to be due to chance, whereas a P value close to 1 suggests no difference between the groups other than due to chance.

- Starting in Spring 2014
- Starting in Summer 2014
- Starting in Autumn 2014
- Starting in Winter 2014

This allowed to make comparison among aging started in different season, but also to take into account the variability linked to each year despite the start of the exposure in the same season (i. e. in this case, summer). The exposure starting in the same season, but in different years was missing in the Cora's study [7].

Ten samples were tested:

- 4 stabilized with two types (Stabilizer A and B) of tin-based stabilization (two at 7 phr TiO$_2$ and two at 9 phr TiO$_2$)
- 6 stabilized with three types (Stabilizer C, D and E) of COS (i. e. Calcium Organic Stabilizer) based stabilization (three at 7 phr TiO$_2$ and three at 9 phr TiO$_2$)

The analysis was developed using graphical evaluations at first, then following a statistical approach in the following sections:

- § 4. 1.: Graphical evaluation of differences due to different starting season
- § 4. 2.: Graphical comparison of Delta E at the end of 48 months exposure to identify differences triggered by different starting season. Although the cyclicity of the Delta E value over exposure time, this value at a precise exposure time is similar to what norms state (e. g. EN 13245-1)
- § 4. 3.: Graphical comparison of the speed to reach the maximum Delta E to identify differences triggered by different starting season or TiO$_2$ loading. The higher this speed (i. e. the higher the Delta E and/or the shorter the time to reach maximum Delta E) the stronger the degradation.
- § 4. 4: Delta E dynamic was analyzed comparing maximum and the minimum values after the start of each exposure. This value is similar to the one used by Cora when focusing on color variation. The reason of this color variation is described above in § 2.2.
- § 4. 5.: Statistical analysis to identify the presence of a significant effect of months of exposure, starting aging season or TiO$_2$ loading on Delta E evolution. Although linear regressions did not provide a good fit for the experimental "undulating" data, they gave an idea of the general tendency to discoloration.
- § 4. 6.: Regression lines vs. months of exposure were drawn considering that starting season and TiO$_2$ loading did not bring to significant effects.
- § 4. 7.: Statistical comparison of the different stabilizers was eventually performed.

3.1. Materials

Samples are manufactured using a typical window profile formulation using PVC SE 950 EG from Shin-Etsu, Calcium Carbonate Tecnofiller from Umbriafiller as filler, Acrylic Impact Modifier KANE ACE FM 50 from KANEKA, Titanium Dioxide Ti-Pure® R-105 from DuPont as pigment. Both Tin-based and COS-based stabilizers are commercial ones from Reagens-Group.

3.2. Formulations

The following formulations were prepared.

3.3. Reparation of test compounds

Test dry-blends were prepared with the recipes shown in Table 1 using a PlasMec laboratory high speed heater and cooler mixer combination.

The following protocol was used for the blending:

- the mixer is run starting ambient temperature and low speed, then all components are added and finally it is switched– switch to high speed
- the material is discharged from heater mixer at 110 °C into cooler mixer
- the material is discharged from cooler mixer at 40 °C

3.4. Extrusion trials

All specimens have been produced using a Krauss Maffei KMD2-25L fully instrumented conical twin-screw extruder at the maximum temperature of the die of 195 °C.

3.5. Outdoor exposure

Natural exposure was carried out according to EN 13245-1 at Reagens plant in San Giorgio di Piano (BO, Italy), southward 45°.
San Giorgio di Piano has:

- typical annual solar irradiance around 5,30 GJ/m2
- average temperature of the warmest month of the year: 25 °C
- severe climate according to EN 12608-1

Color have been measured with an X-Rite SP 62 colorimeter working at D65/10 according to EN 13245-1.
Statistical data elaboration has been performed with Statgraphics Centurion XVII.

4. Results and discussion

Delta E data are recorded in function of the irradiation (Klys) and months of exposure. All the discussion was performed on data plotted against months of exposure, but may be repeated on data plotted against irradiation (KLys) with the same conclusions.

Overall, Delta E is mainly due to L* variation, but only in the case of Tin stabilized samples, also to b* ones (see Fig. 7). From Fig. 7, it is also evident how the color of a sample exposed outdoor increases and decreases with time as outlined in § 2. 2. and in particular in Fig. 3.

4.1. Comparison of data on a graphical basis

From Fig. 7, graphically comparing data of aging started in the different seasons and in the same season (summer in two different years), it is not evident a starting season that particularly negatively affects the aging. This evaluation does not point out a clear variability in the cycle's maxima and minima in function of starting season as, instead, evidenced by Cora. Apart from few cases, it is not graphically evident a positive effect of the increase of TiO$_2$ loading from 7 to 9 phr.

4.2. Comparison at end exposure – 48 months

The degree of degradation is evaluated at the end of the exposure: as illustrated in Fig. 8, plotting the Detla E after 48 months of exposure, it seems to be a general worsening of the color when tests start in spring and winter than in summer and autumn. (despite exceptions for Tin stabilized samples). In particular, in Fig. 8, the values of Delta E of all COS samples whose exposure is started in Summer 2013, Summer 2014, Autumn 2014 are lower than the values of the same samples started in Spring 2014 and Winter 2014. This is not in line with Cora's conclusions.

From this analysis, it seems that all stabilizers, but Tin stabilizer A (and maybe Tin stabilizer B), perform similarly.

Table 1
Formulations (parts w/w).

|	13REAfa3 Tin A/9 TiO2	13REAfa4 Tin A/7 TiO2	13REAfa5 Tin B/9 TiO2	13REAfa6 Tin B/7 TiO2	13REAfa7 COS C/9 TiO2	13REAfa8 COS C/7 TiO2	13REAfa9 COS D/9 TiO2	13REAfa10 COS D/7 TiO2	13REAfa11 COS E/9 TiO2	13REAfa12 COS E/7 TiO2
PVC	100	100	100	100	100	100	100	100	100	100
Calcium carbonate	6	6	6	6	6	6	6	6	6	6
Acrylic Impact Modifier	5	5	5	5	5	5	5	5	5	5
Titanium Dioxide	9	7	9	7	9	7	9	7	9	7
Tin-based stabilization A	3	3								
Tin-based stabilization B			3	3						
COS-based stabilization C					4	4				
COS-based stabilization D							4	4		
COS-based stabilization E									4	4
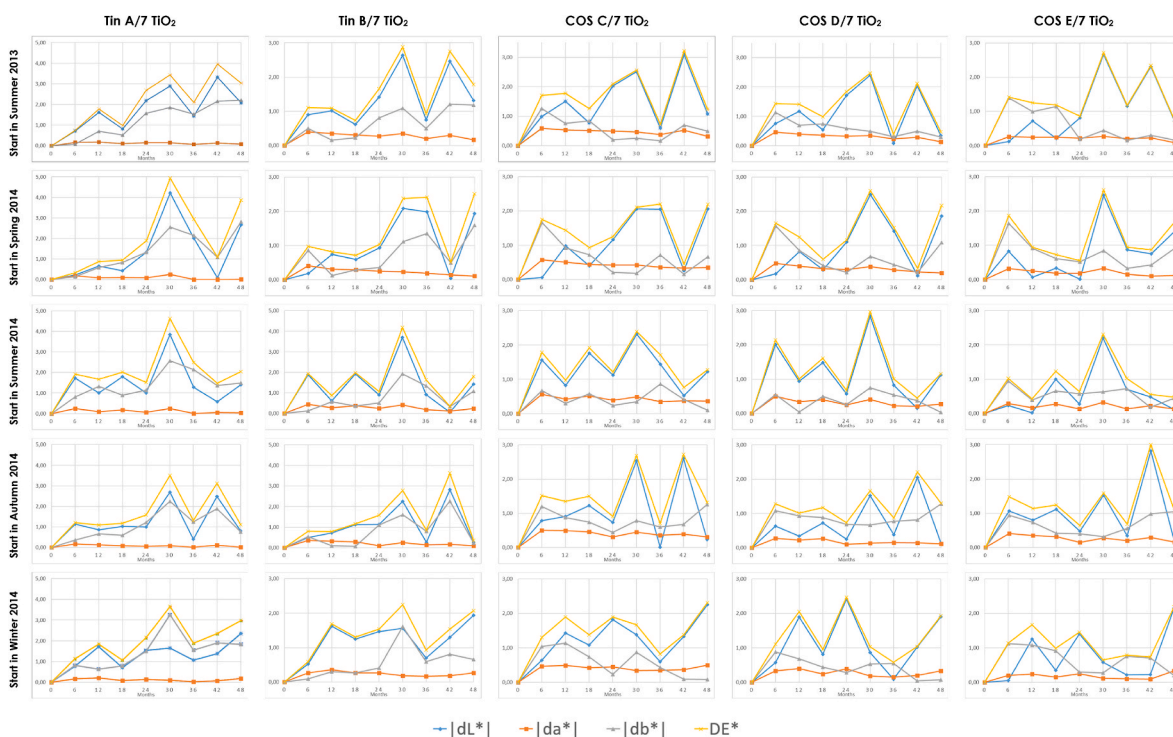
Fig. 7. Comparison between DE and |DL*|, |Da*|, |Db*| vs. months of exposure in formulations with 7 phr TiO$_2$ (start in Summer 2013 vs Spring 2014 vs Summer 2014 vs Autumn 2014 vs Winter 2014).

4.3. Comparison of color speed change to maximum

This Section deals with an evaluation based on the rate to reach the maximum discoloration. Thus, focusing only on the maximum Delta E reached by each sample in each exposure condition and on the time needed to reach it, a line was drawn from Delta E = 0 to the point of maximum Delta E excluding all the other data: an example of this elaboration is shown in Fig. 9 where the full line is for experimental data and the dashed line is the one drawn from Delta E = 0 to the point maximum Delta E. Fig. 10 shows two examples relevant to Stabilizer COS C and Stabilizer COS D at 7 phr of TiO$_2$, while the data on the other stabilizer are presented in Appendix (Fig. 17).

4. 3. 1. Effect of starting season
From Fig. 10, there seems to be no association between maximum color speed change vs. season of exposure. In particular it seems not

possible to definitively identify one single season start affecting the discoloration more than the others.

4. 3. 2. Effect of TiO$_2$ loading
Excluding the influence of the starting season (as it seems from § 4. 3. 1.), the lines described in § 4. 3. 1. were drawn (but considering an average slope of all starting seasons for each sample). From Table 2, an increase of TiO$_2$ loading from 7 to 9 phr has not always a better protection effect.

4.4. Amplitude of colour change

Amplitude of color change is an indication of the extent of the degradation cycle made up of discoloration/oxidation/photobleaching. Indeed, Cora reported that amplitude of cyclic color change should be taken into account to ascertain the degree of degradation. To this end,
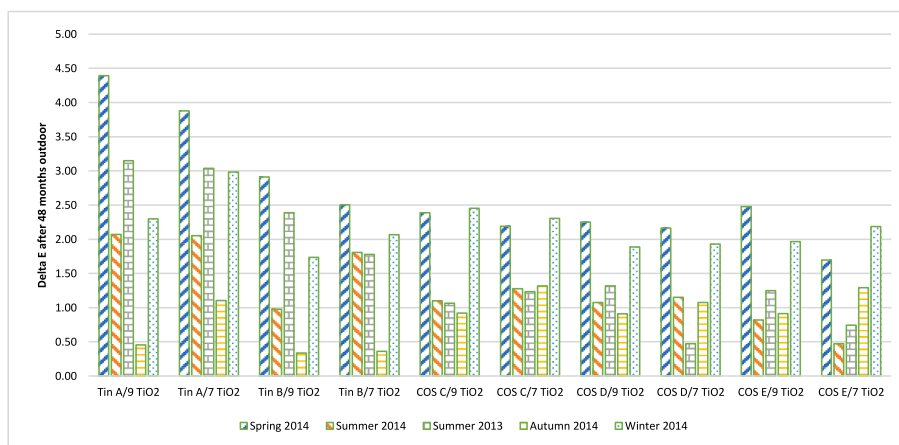
Fig. 8. Delta E after 48 months exposure starting in different seasons.
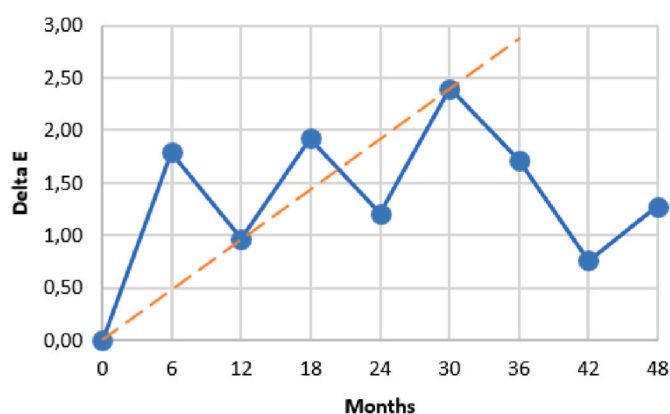

Fig. 9. Example of experimental data (full line) and line from Delta E = 0 to the point of maximum Delta E (dashed line).

the amplitude of Delta E was calculated between the maximum and the minimum Delta E after the start of each exposure (Table 3). It is noteworthy the variability also in the same starting season but in different years (e. g. sample Tin B at 7 phr of TiO_2 (Tin B/7 TiO_2), or sample COS E at 9 phr TiO_2 (COS E/9 TiO_2) in Summer 2013 and Summer 2014).

Generally (but not always, e. g. sample Tin A at 7 phr of TiO_2 (Tin A/7 TiO_2), COS C at 9 phr of TiO_2 (COS C/9 TiO_2), COS D at 9 phr TiO_2 (COS D/9 TiO_2), COS E at 7 phr TiO_2 (COS E/7 TiO_2)), the lowest amplitude of cyclic color change seems to be obtained when exposure program starts in winter. Also in this case, it is in contrast with Cora that stated that "the lowest total color difference is obtained when exposure program starts in autumn and the highest total color difference is observed when exposure starts in winter".

It is also evident that large amplitudes in Delta E are not always correlated to lower TiO_2 levels.

4.5. Multiple regression analysis and comparison of regression lines

In order to further develop the analysis reported in § 4. 1., 4. 2. and § 4. 3. and to further investigate the variables influencing Delta E, a multiple regression analysis was run comparing different specifications, starting from the simplest, based only on starting season, or TiO_2 loading and gradually including more variables, such as exposure months, up to the more general model, in which the explanatory variables are starting season, exposure months and TiO_2 loading.

4.5.1. Multiple regression analysis by starting season

The simplest multiple regression analysis was, then, performed on all

data considering Delta E vs. starting season including all the 5 exposures (in each season of 2014 and summer 2013). Table 4 reports results for COS stabilizer C and D at 7 phr of TiO_2 with summer 2013 as reference season. The results related of the other samples and with the other seasons as reference ones, are in Appendix (Table 8, Table 9, Table 10, Table 11, Table 12). The analysis was repeated five times considering a different season as reference each time, but the results confirmed each time the same conclusion: since the P-value is greater or equal to 0,05, that term is not statistically significant at the 5,0% level.

4.5.2. Multiple regression analysis by TiO_2 loading

Another simple multiple regression analysis was, then, performed on Delta E vs. TiO_2 loading, (in each season of 2014 and summer 2013). Since the P-value is greater or equal to 0,05 (Table 5), that term is not statistically significant at the 5,0% level.

The same analysis was run translating 9 and 7 phr of TiO_2 into a dummy variable 1 and 0 respectively in order to further assess the presence of TiO_2 loading related effects, but, also in this case, that term is not statistically significant at the 5,0% level (Table 6).

4.5.3. Multiple regression analysis by months, starting season, TiO_2 loading

The more complete multiple regression analysis (including months of exposure, starting season, TiO_2 loading as the explanatory variables), generally confirmed that starting season and TiO_2 loading were not significant at the 5,0% level.[2] In this case, only one reference season was taken into account (i. e. Summer 2013, Table 7) as it was evident, from § 4. 5. 1., that similar results would have been obtained taking all the other starting seasons as reference.

4.6. Model simplification

The analysis carried out in § 4. 5., triggers that at least one of those predictor variables could be removed without hurting the model significantly. It would be wrong at this point to assume that all 2 predictor variables with P-values above 0,05 (i. e. TiO_2 and Starting season) could be removed. Due to the high multicollinearity in the data, all P-values may change dramatically if even one variable is removed from the model. A stepwise regression was used for simplifying the model. In a stepwise regression, variables are added or removed from a regression model one at a time, with the goal of obtaining a model that contains only significant predictors but does not exclude any useful variables.

This stepwise regression removed the 2 predictor variables that had

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[2] Actually, Autumn staring season is significant at the 5,0% level for Tin A/9 TiO_2| Tin A/7 TiO_2, but, as this significance is not present in all the other samples, it has to be ruled out as a general rule for PVC weathering.
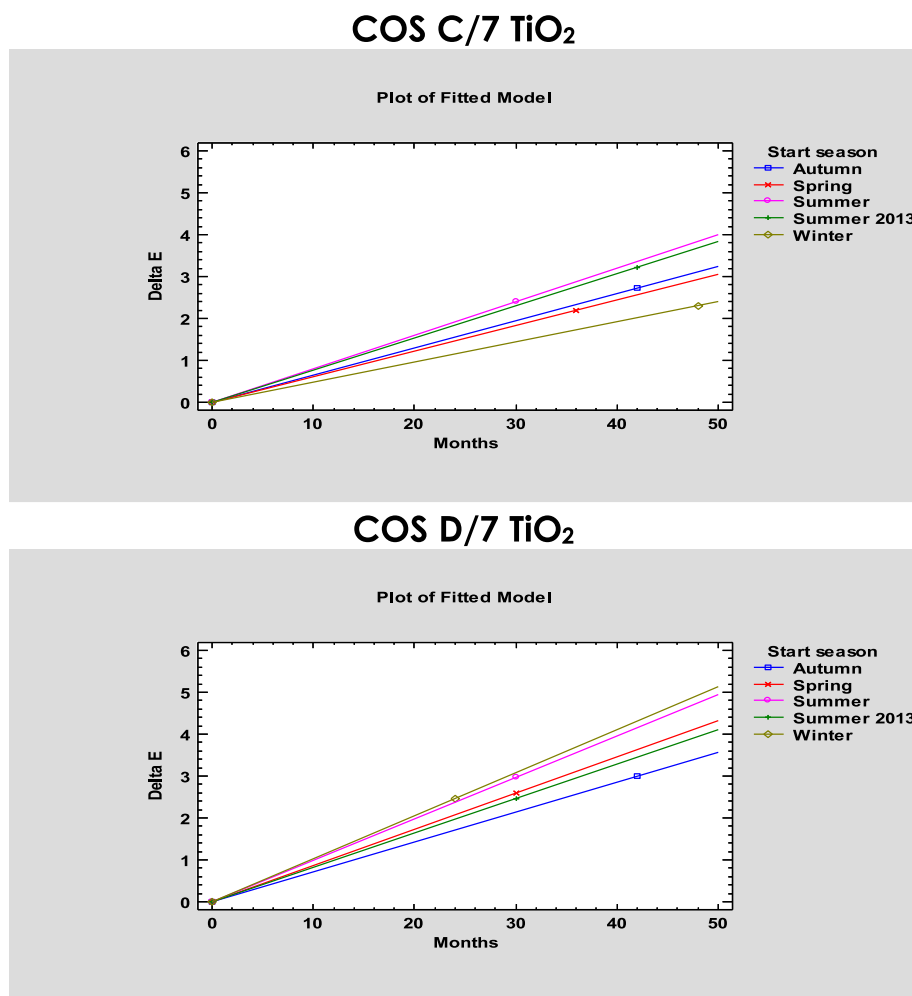
Fig. 10. Evolution of maximum color speed change for samples COS C/7 TiO2 and COS D/7 TiO2 exposed starting in different seasons. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Table 2
Comparison of maximum color speed change vs. TiO2 loading for each stabilizer.

TiO$_2$ (phr)	Type	Slope
9	Tin A	0,1
7	Tin A	0,13
9	Tin B	0,08
7	Tin B	0,09
7	COS C	0,08
9	COS C	0,07
9	COS D	0,1
7	COS D	0,09
9	COS E	0,11
7	COS E	0,07

Tin stabilizer A has a slope far higher than the other ones, thus, it is evident that all the stabilizers provide similar performance, while Tin stabilizer A provides a significantly worse one.

It has to be pointed out that the linear regression, of course, did not well fit the experimental "undulating" data, but was a way to have an idea of the tendency to discoloration. In addition, due to the bad fit, an analysis of the outliers was not performed as it would have been not significant.

4.7. Comparison of regression lines

Considering that starting season and TiO$_2$ loading were not significant (§ 4. 6.), an analysis was performed to understand if some stabilizer type (e. g. Tin stabilizer A identified in § 4. 6.) was significantly less effective than the others. To this aim, a comparison of regression lines was performed (including the data at all starting season and TiO$_2$ loading for each stabilization type).

Because the P-value for the regression coefficient is less than 0,01, there are statistically significant differences among the regression coefficients for the various values of samples at the 99% confidence level. Fig. 13 visually suggests that the Tin stabilizer A at 9 phr TiO$_2$ (Tin A/9 TiO$_2$) and at 7 phr TiO$_2$ (Tin A/7 TiO$_2$) are the significantly different ones.

To confirm this, other comparisons of regression lines were performed:

P-values above 0,05 (starting season and TiO$_2$ loading) allowing to draw simple regression lines for each stabilizer shown in Fig. 11.

Furthermore, considering that Delta E is 0 at Months = 0, it is possible to force equal intercepts considering all data independently on the starting season and TiO$_2$ loading Fig. 12). In Fig. 12, only the line of

Table 3
Comparison of Delta E amplitude of color change.

TiO$_2$ (phr)	Code	Summer 2103	Spring 2014	Summer 2014	Autumn 2014	Winter 2014
9	Max/Min- Tin A/9 TiO$_2$	4,59	4,09	2,94	2,95	1,97
7	Max/Min- Tin A/7 TiO$_2$	3,22	4,61	3,15	2,41	2,59
9	Max/Min- Tin B/9 TiO$_2$	2,16	2,2	2,7	2,3	1,05
7	Max/Min- Tin B/7 TiO$_2$	2,15	1,99	3,84	3,26	1,66
9	Max/Min- COS C/9 TiO$_2$	1,61	2,15	2,6	3,01	1,92
7	Max/Min- COS C/7 TiO$_2$	2,49	1,75	1,64	2,02	1,49
9	Max/Min- COS D/9 TiO$_2$	1,52	2,2	2,61	1,61	1,55
7	Max/Min- COS D/7 TiO$_2$	2,08	2,27	2,51	2,36	1,89
9	Max/Min- COS E/9 TiO$_2$	1,65	3	3	1,72	1,43
7	Max/Min- COS E/7 TiO$_2$	1,97	2,07	1,88	1,48	1,54

Table 4
Significance for starting season vs. Summer 2013.

	Variable	Contribution to Delta E	P-Value
COS C/7 TiO2	Autumn 2014	−0,2100	0,5859
	Winter 2014	−0,2189	0,5702
	Spring 2014	−0,2523	0,5133
	Summer 2014	−0,2844	0,4613
COS D/7 TiO2	Autumn 2014	−0,0289	0,9422
	Winter 2014	0,0044	0,9911
	Spring 2014	0,0178	0,9644
	Summer 2014	−0,0122	0,9755

Table 5
Significance for TiO$_2$ loading.

	Variable	Contribution to Delta E	P-Value
Tin A/9 TiO2| Tin A/7 TiO2	TiO$_2$	−0,0961	0,4697
Tin B/9 TiO2| Tin B/7 TiO2	TiO$_2$	−0,0401	0,6789
COS C/9 TiO2| COS C/7 TiO2	TiO$_2$	0,0220	0,7992
COS D/9 TiO2| COS D/7 TiO2	TiO$_2$	0,0363	0,6633
COS E/9 TiO2| COS E/7 TiO2	TiO$_2$	0,0443	0,5805

Table 6
Significance for TiO$_2$ loading (dummy variable 0, 1).

	Variable	Contribution to Delta E	P-Value
Tin A/9 TiO2| Tin A/7 TiO2	TiO$_2$	−0,1922	0,4697
Tin B/9 TiO2| Tin B/7 TiO2	TiO$_2$	−0,0802	0,6789
COS C/9 TiO2| COS C/7 TiO2	TiO$_2$	−0,0787	0,6491
COS D/9 TiO2| COS D/7 TiO2	TiO$_2$	0,0727	0,6633
COS E/9 TiO2| COS E/7 TiO2	TiO$_2$	0,0887	0,5805

Table 7
Significance for months of exposure, starting season, TiO$_2$ loading vs. Summer 2013.

	Variable	Contribution to Delta E	P-Value
Tin A/9 TiO2| Tin A/7 TiO2	Month	0,0535	0,0000
	TiO$_2$	−0,0961	0,3287
	Autumn 2014	−0,7694	0,0149[a]
	Winter 2014	−0,3439	0,2695
	Spring 2014	−0,3078	0,3226
	Summer 2014	−0,3561	0,2529
Tin B/9 TiO2| Tin B/7 TiO2	Month	0,0301	0,0000
	TiO$_2$	−0,0401	0,6366
	Autumn 2014	−0,2633	0,3277
	Winter 2014	−0,2539	0,3452
	Spring 2014	−0,1350	0,6151
	Summer 2014	−0,1433	0,5935
COS C/9 TiO2| COS C/7 TiO2	Month	0,0199	0,0003
	TiO$_2$	0,0220	0,7876
	Autumn 2014	−0,2139	0,4084
	Winter 2014	−0,2450	0,3439
	Spring 2014	−0,2211	0,3928
	Summer 2014	−0,2656	0,3052
COS D/9 TiO2| COS D/7 TiO2	Month	0,0158	0,0033
	TiO$_2$	0,0363	0,6542
	Autumn 2014	−0,2372	0,3560
	Winter 2014	−0,1856	0,4698
	Spring 2014	−0,0939	0,7143
	Summer 2014	−0,0956	0,7094
COS E/9 TiO2| COS E/7 TiO2	Month	0,0186	0,0002
	TiO$_2$	0,0443	0,5560
	Autumn 2014	−0,2567	0,2822
	Winter 2014	−0,2228	0,3502
	Spring 2014	−0,0989	0,6778
	Summer 2014	−0,2933	0,2196

[a] Significant at the 5,0% level.

- including only the samples different from the ones with Tin stabilizer A (from Tin B/9 TiO$_2$- to COS E/7 TiO$_2$): in this case, because the P-value for the regression coefficient is greater than or equal to 0,05, there are not statistically significant differences among the regression coefficients for the various values of samples at the 5% level. This is also visually evident from Fig. 14.

- including the samples different from the ones with Tin stabilizer A at 9 phr TiO$_2$ (from Tin B/9 TiO$_2$- to COS E/7 TiO$_2$): in this case, because the P-value for the regression coefficient is less than 0,01, there are statistically significant differences among the regression coefficients for the various samples at the 99% confidence level. It is

thus evident (also visually from Fig. 15) that the sample with Tin stabilizer A at 9 phr TiO$_2$ (Tin A/7 TiO$_2$) is the significantly different one.
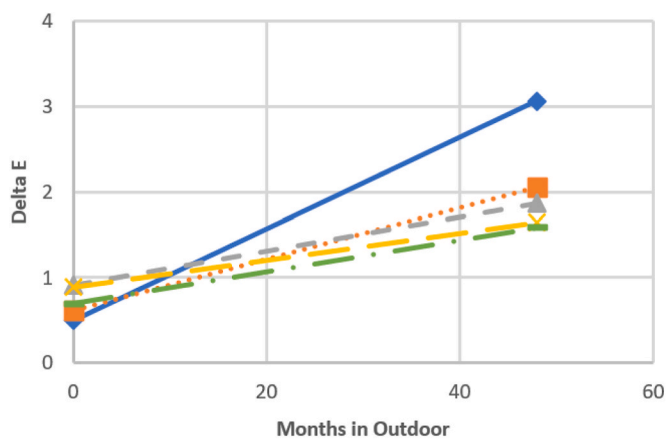
Fig. 11. Linear regression excluding not statistically significant parameters (intercept different from 0).
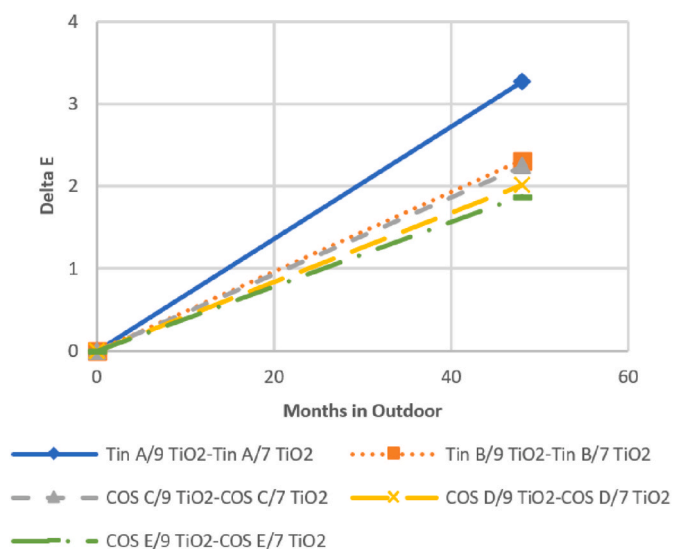

Fig. 12. Linear regression excluding not statistically significant parameters (intercept = 0).
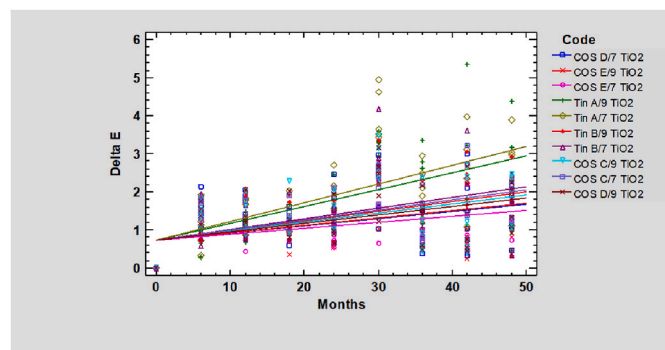

Fig. 13. Comparison of regression lines with all tested samples.
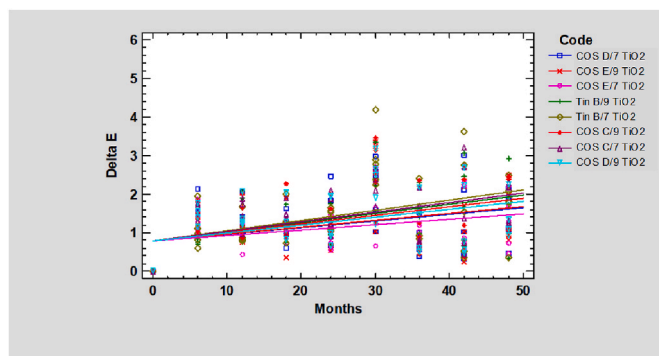
Fig. 14. Comparison of regression lines with all tested samples, but Tin stabilizer A at 7 and 9 phr of TiO_2 ones.
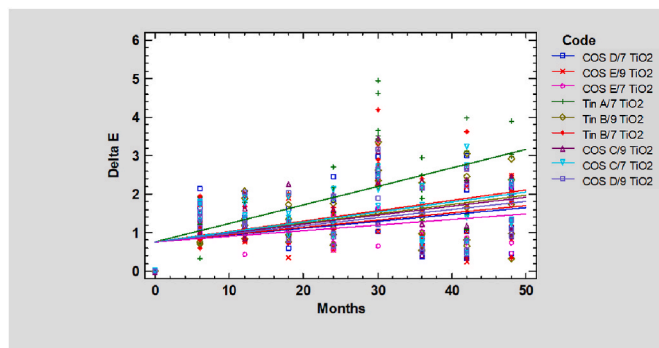
Fig. 15. Comparison of regression lines with all tested samples, but Tin stabilizer A at 9 phr of TiO2 one.

- Including the samples different from the ones with Tin stabilizer A at 7 phr TiO_2 (Tin A/9 TiO_2 and from Tin B/9 TiO_2- to COS E/7 TiO_2): in this case, because the P-value for the regression coefficient is less than 0,01, there are statistically significant differences among the regression coefficients for the various samples at the 99% confidence level. It is thus evident (also visually from Fig. 16) that the samples with Tin stabilizer A at 7 phr TiO_2 (Tin A/9 TiO_2) is the significantly different one.

In Figs. 13–16, only the lines of Tin stabilizer A have a slope far higher the other ones, thus, it is evident that all the stabilizers provide similar performance, while Tin stabilizer A provides a significantly worse one.

Fig. 16. Comparison of regression lines with all tested samples, but Tin stabilizer A at 7 phr of TiO_2 one.

5. Conclusions
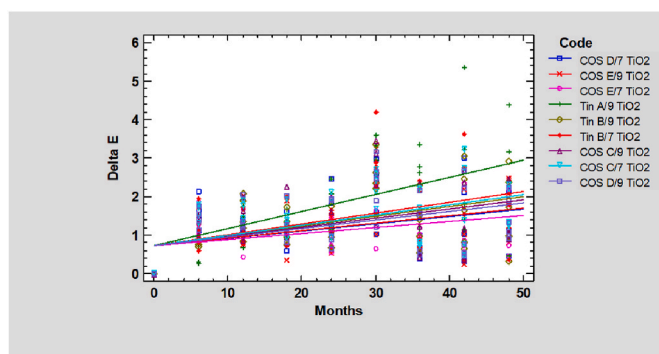
Both comparison of data on a graphical basis (§ 4. 1. - 4. 4.) and statistical analysis of data (§ 4. 5.) confirmed that starting season has not a significant effect on discoloration.

As for TiO_2 loading effect, an initial graphical evaluation of data (§ 4. 1. - 4. 4.) and a statistical analysis (§ 4. 5.) suggests that the increase of TiO_2 from 7 to 9 phr has not a significant effect.

A statistical analysis (§ 4. 6. - 4. 7.) showed a significant lower stabilization efficiency for Tin stabilizer A, while all the others performed in a similar statistical way. In any case, almost all stabilizers perform in line with the requirements of EN 13245-1 for a codification at least N,21,25[3] maintaining a delta E < 4 at the end of 4 years exposure.

CRediT author statement

Gardi Stefano (GS): Conceptualization, Methodology/Study design, software, Formal analysis, Investigation, Data curation, Writing – original draft, Giannone Lorenzo (GL): Methodology/Study design, Formal analysis, Investigation, Data curation, Writing – review and editing, Visualization, Sarti Gianfranco (SGf): Conceptualization, Methodology/ Study design, Validation, Formal analysis, Investigation, Data curation, Writing – review and editing, Project administration, Sarti Gianluca (SGl): Conceptualization, Methodology/Study design, Validation, Formal analysis, Investigation, Data curation, Writing – review and editing, Supervision, Costa Michele (CM): Methodology/Study design, Software, Validation, Formal analysis, Investigation, Data curation, Writing – review and editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgment

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.polymertesting.2023.108123.

Appendix

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[3] N = Natural Aging; Radiant exposure 4 years * 5,30 GJ/m2/year = 21 GJ/m2; Average temperature of the warmest month of the year = 25 °C.

Tin A/9 TiO₂

Tin A/7 TiO₂

Tin B/9 TiO₂

Tin B/7 TiO₂

COS C/9 TiO₂

COS D/9 TiO₂

COS E/9 TiO₂

COS E/7 TiO2
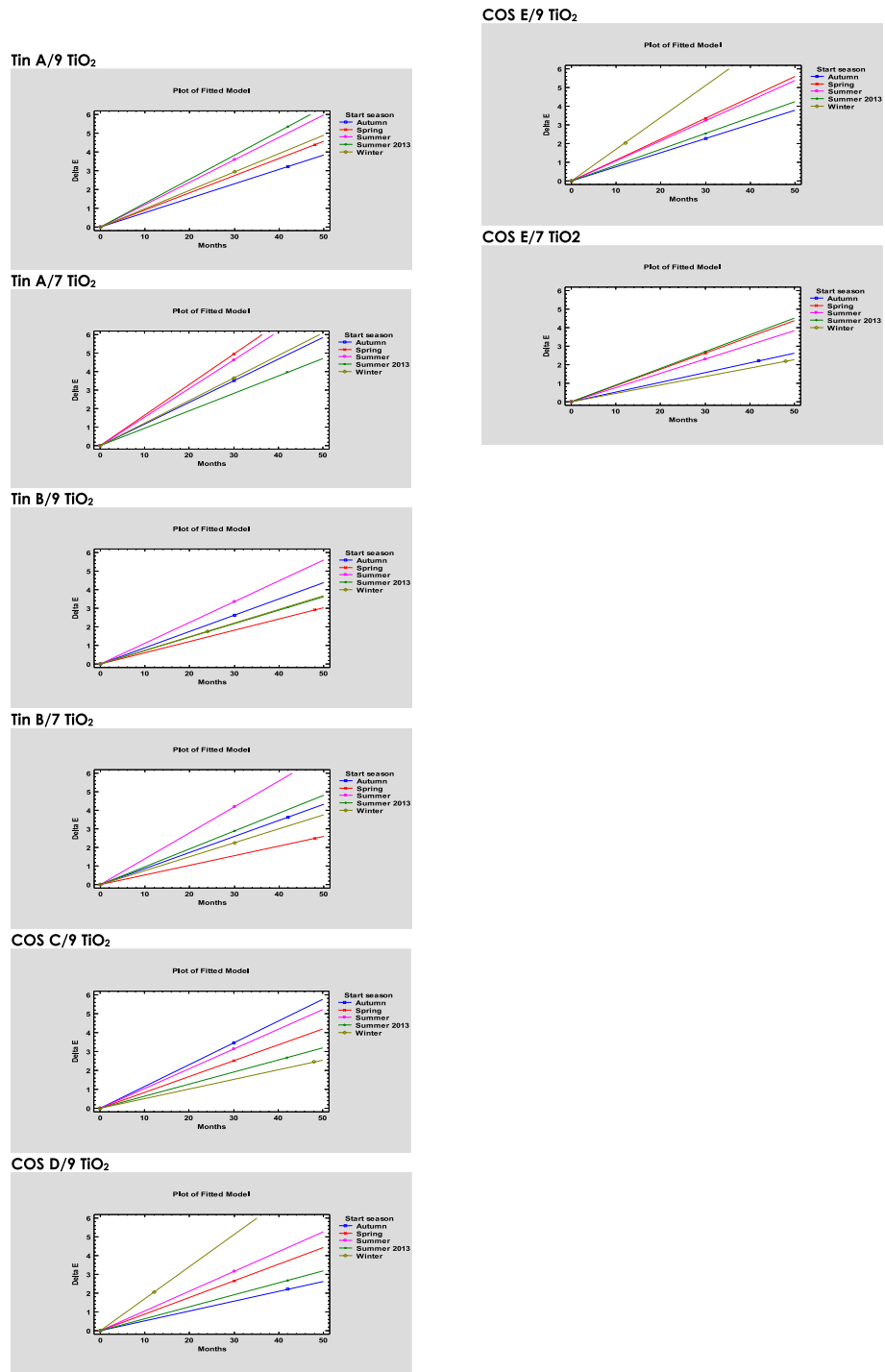
Fig. 17. Evolution of maximum Delta E for each semple exposed starting in different seasons

Table 8
Significance for starting season vs. Summer 2013

	Variable	Contribution to Delta E	P-Value
Tin A/9 TiO2	Autumn 2014	−1,0222	0,0967
	Winter 2014	−0,5011	0,4093
	Spring 2014	−0,4111	0,4979
	Summer 2014	−0,6067	0,3188
Tin A/7 TiO2	Autumn 2014	−0,5167	0,4040
	Winter 2014	−0,1867	0,7621

Table 8 (*continued*)

	Variable	Contribution to Delta E	P-Value
	Spring 2014	−0,2044	0,7403
	Summer 2014	−0,1056	0,8641
Tin B/9 TiO2	Autumn 2014	−0,4189	0,3198
	Winter 2014	−0,3967	0,3458
	Spring 2014	−0,0911	0,8277
	Summer 2014	−0,3922	0,3512
Tin B/7 TiO2	Autumn 2014	−0,1078	0,8223
	Winter 2014	−0,1111	0,8169
	Spring 2014	−0,1789	0,7094
	Summer 2014	0,1056	0,8259
COS C/9 TiO2	Autumn 2014	−0,2178	0,6060
	Winter 2014	−0,2711	0,5212
	Spring 2014	−0,1900	0,6526
	Summer 2014	−0,2467	0,5593
COS D/9 TiO2	Autumn 2014	−0,4456	0,2428
	Winter 2014	−0,3756	0,3237
	Spring 2014	−0,2056	0,5875
	Summer 2014	−0,1789	0,6367
COS E/9 TiO2	Autumn 2014	−0,3511	0,3855
	Winter 2014	−0,2156	0,5931
	Spring 2014	−0,0356	0,9296
	Summer 2014	−0,1422	0,7242
COS E/7 TiO2	Autumn 2014	−0,1622	0,6300
	Winter 2014	−0,2300	0,4952
	Spring 2014	−0,1622	0,6300
	Summer 2014	−0,4444	0,1910

Table 9
Significance for starting season vs. Autumn 2014

	Variable	Contribution to Delta E	P-Value
Tin A/9 TiO2	Winter 2014	0,5211	0,3911
	Spring 2014	0,6111	0,3153
	Summer 2014	0,4156	0,4933
	Summer 2013	1,0222	0,0967
Tin A/7 TiO2	Winter 2014	0,3300	0,5931
	Spring 2014	0,3122	0,6131
	Summer 2014	0,4111	0,5060
	Summer 2013	0,5167	0,4040
Tin B/9 TiO2	Winter 2014	0,0222	0,9576
	Spring 2014	0,3278	0,4352
	Summer 2014	0,0267	0,9492
	Summer 2013	0,4189	0,3198
Tin B/7 TiO2	Winter 2014	−0,0033	0,9945
	Spring 2014	−0,0711	0,8822
	Summer 2014	0,2133	0,6569
	Summer 2013	0,1078	0,8223
COS C/9 TiO2	Winter 2014	−0,0533	0,8993
	Spring 2014	0,0278	0,9475
	Summer 2014	−0,0289	0,9454
	Summer 2013	0,2178	0,6060
COS C/7 TiO2	Winter 2014	−0,0089	0,9816
	Spring 2014	−0,0422	0,9126
	Summer 2014	−0,0744	0,8466
	Summer 2013	0,2100	0,5859
COS D/9 TiO2	Winter 2014	0,0700	0,8532
	Spring 2014	0,2400	0,5268
	Summer 2014	0,2667	0,4821
	Summer 2013	0,4456	0,2428
COS D/7 TiO2	Winter 2014	0,0333	0,9333
	Spring 2014	0,0467	0,9068
	Summer 2014	0,0167	0,9666
	Summer 2013	0,0289	0,9422
COS E/9 TiO2	Winter 2014	0,1356	0,7366
	Spring 2014	0,3156	0,4350
	Summer 2014	0,2089	0,6046
	Summer 2013	0,3511	0,3855
COS E/7 TiO2	Winter 2014	−0,0678	0,8403
	Spring 2014	0,0000	1,0000
	Summer 2014	−0,2822	0,4034
	Summer 2013	0,1622	0,6300

Table 10
Significance for starting season vs. Winter 2014

	Variable	Contribution to Delta E	P-Value
Tin A/9 TiO2	Autumn 2014	−0,5211	0,3911
	Spring 2014	0,0900	0,8817
	Summer 2014	−0,1056	0,8615
	Summer 2013	0,5011	0,4093
Tin A/7 TiO2	Autumn 2014	−0,3300	0,5931
	Spring 2014	−0,0178	0,9770
	Summer 2014	0,0811	0,8953
	Summer 2013	0,1867	0,7621
Tin B/9 TiO2	Autumn 2014	−0,0222	0,9576
	Spring 2014	0,3056	0,4667
	Summer 2014	0,0044	0,9915
	Summer 2013	0,3967	0,3458
Tin B/7 TiO2	Autumn 2014	0,0033	0,9945
	Spring 2014	−0,0678	0,8876
	Summer 2014	0,2167	0,6519
	Summer 2013	0,1111	0,8169
COS C/9 TiO2	Autumn 2014	0,0533	0,8993
	Spring 2014	0,0811	0,8474
	Summer 2014	0,0244	0,9538
	Summer 2013	0,2711	0,5212
COS C/7 TiO2	Autumn 2014	0,0089	0,9816
	Spring 2014	−0,0333	0,9310
	Summer 2014	−0,0656	0,8647
	Summer 2013	0,2189	0,5702
COS D/9 TiO2	Autumn 2014	−0,0700	0,8532
	Spring 2014	0,1700	0,6535
	Summer 2014	0,1967	0,6037
	Summer 2013	0,3756	0,3237
COS D/7 TiO2	Autumn 2014	−0,0333	0,9333
	Spring 2014	0,0133	0,9733
	Summer 2014	−0,0167	0,9666
	Summer 2013	−0,0044	0,9911
COS E/9 TiO2	Autumn 2014	−0,1356	0,7366
	Spring 2014	0,1800	0,6553
	Summer 2014	0,0733	0,8555
	Summer 2013	0,2156	0,5931
COS E/7 TiO2	Autumn 2014	0,0678	0,8403
	Spring 2014	0,0678	0,8403
	Summer 2014	−0,2144	0,5247
	Summer 2013	0,2300	0,4952

Table 11
Significance for starting season vs. Spring 2014

	Variable	Contribution to Delta E	P-Value
Tin A/9 TiO2	Autumn 2014	−0,6111	0,3153
	Winter 2014	−0,0900	0,8817
	Summer 2014	−0,1956	0,7466
	Summer 2013	0,4111	0,4979
Tin A/7 TiO2	Autumn 2014	−0,3122	0,6131
	Winter 2014	0,0178	0,9770
	Summer 2014	0,0989	0,8726
	Summer 2013	0,2044	0,7403
Tin B/9 TiO2	Autumn 2014	−0,3278	0,4352
	Winter 2014	−0,3056	0,4667
	Summer 2014	−0,3011	0,4732
	Summer 2013	0,0911	0,8277
Tin B/7 TiO2	Autumn 2014	0,0711	0,8822
	Winter 2014	0,0678	0,8876
	Summer 2014	0,2844	0,5540
	Summer 2013	0,1789	0,7094
COS C/9 TiO2	Autumn 2014	−0,0278	0,9475
	Winter 2014	−0,0811	0,8474
	Summer 2014	−0,0567	0,8931
	Summer 2013	0,1900	0,6526
COS C/7 TiO2	Autumn 2014	0,0422	0,9126
	Winter 2014	0,0333	0,9310
	Summer 2014	−0,0322	0,9333
	Summer 2013	0,2522	0,5133
COS D/9 TiO2	Autumn 2014	−0,2400	0,5268
	Winter 2014	−0,1700	0,6535

Table 11 (*continued*)

	Variable	Contribution to Delta E	P-Value
	Summer 2014	0,0267	0,9438
	Summer 2013	0,2056	0,5875
COS D/7 TiO2	Autumn 2014	−0,0467	0,9068
	Winter 2014	−0,0133	0,9733
	Summer 2014	−0,0300	0,9400
	Summer 2013	−0,0178	0,9644
COS E/9 TiO2	Autumn 2014	−0,3156	0,4350
	Winter 2014	−0,1800	0,6553
	Summer 2014	−0,1067	0,7912
	Summer 2013	0,0356	0,9296
COS E/7 TiO2	Autumn 2014	0,0000	1,0000
	Winter 2014	−0,0678	0,8403
	Summer 2014	−0,2822	0,4034
	Summer 2013	0,1622	0,6300

Table 12
Significance for starting season vs. Summer 2014

	Variable	Contribution to Delta E	P-Value
Tin A/9 TiO2	Autumn 2014	−0,4156	0,4933
	Winter 2014	0,1056	0,8615
	Spring 2014	0,1956	0,7466
	Summer 2013	0,6067	0,3188
Tin A/7 TiO2	Autumn 2014	−0,4111	0,5060
	Winter 2014	−0,0811	0,8953
	Summer 2014	−0,0989	0,8726
	Summer 2013	0,1056	0,8641
Tin B/9 TiO2	Autumn 2014	−0,0267	0,9492
	Winter 2014	−0,0044	0,9915
	Summer 2014	0,3011	0,4732
	Summer 2013	0,3922	0,3512
Tin B/7 TiO2	Autumn 2014	−0,2133	0,6569
	Winter 2014	−0,2167	0,6519
	Summer 2014	−0,2844	0,5540
	Summer 2013	−0,1056	0,8259
COS C/9 TiO2	Autumn 2014	0,0289	0,9454
	Winter 2014	−0,0244	0,9538
	Summer 2014	0,0567	0,8931
	Summer 2013	0,2467	0,5593
COS C/7 TiO2	Autumn 2014	0,0744	0,8466
	Winter 2014	0,0656	0,8647
	Summer 2014	0,0322	0,9333
	Summer 2013	0,2844	0,4613
COS D/9 TiO2	Autumn 2014	−0,2667	0,4821
	Winter 2014	−0,1967	0,6037
	Summer 2014	−0,0267	0,9438
	Summer 2013	0,1789	0,6367
COS D/7 TiO2	Autumn 2014	−0,0167	0,9666
	Winter 2014	0,0167	0,9666
	Summer 2014	0,0300	0,9400
	Summer 2013	0,0122	0,9755
COS E/9 TiO2	Autumn 2014	−0,2089	0,6046
	Winter 2014	−0,0733	0,8555
	Summer 2014	0,1067	0,7912
	Summer 2013	0,1422	0,7242
COS E/7 TiO2	Autumn 2014	0,2822	0,4034
	Winter 2014	0,2144	0,5247
	Summer 2014	0,2822	0,4034
	Summer 2013	0,4444	0,1910

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