

# Intrinsic Differences on the Photodegradation Mechanisms between Pigmented- and Non-Pigmented Coatings in terms of Multi-Scale Analysis

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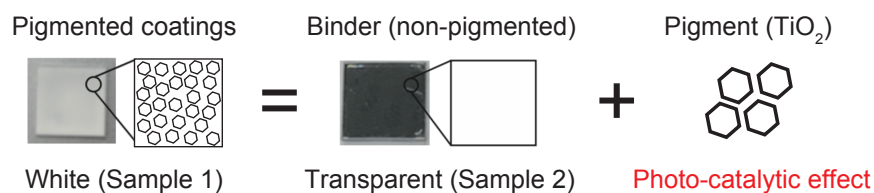
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## 1 Introduction and Methodologies

Durability of surface protective coatings is a one of the most critical aspects for long-term qualities with respect to buildings and infrastructures. Thus, an establishment of appropriate evaluation procedure are strongly required. In order to assess degradation grades for polymeric materials, Carbonyl index (CI) is the most commonly applied indicator to evaluate degradation. However, CI may be not appropriate to evaluate degradation level, in particular physical properties, because macroscopic properties mostly related with material internal morphology (*e.g.*, macromolecular architecture, pore structure, configuration of fillers). In this study, multi-scale degradation analysis of photodegradation are conducted for pigmented coating containing acrylic urethane + TiO<sub>2</sub> pigment and for non-pigmented coating containing only acrylic urethane for discussing the intrinsic differences in the photodegradation mechanism between the pigmented and non-pigmented coatings and the effect of the interface between the pigment and the binder (as shown in Figure 1.).

Ultraviolet (UV) irradiation (180W/m<sup>2</sup> @ 300-400nm) was performed using our lab-built UV irradiation equipment, reported in (Ishida *et al.* 2019). Photo-aging tests were conducted under 60°C at surface temperature and at a low relative humidity (RH) condition (<10%). The results of Fourier transform infrared spectroscopy (FTIR), solvent swelling experiments, ultrasonic measurements of elastic moduli, and colourimetry used for material characterisation before and after photo-aging.



**Figure 1.** Composition of sample coatings.

**Table 1.** Sammarization of property changes before and after photo-aging in terms of multi-scale perspective.

		Prior to aging	After 300 h aging	Change ratio
Carbonyl Index ratio: $CI(t)/CI(t = 0)$	Sample 1	1.00	4.48	+338 [%]
	Sample 2	1.00	4.32	+332 [%]
Elastic modulus [MPa]	Sample 1	1744.98	2205.59	+26.4 [%]
	Sample 2	43.58	833.90	+19.1 [%]
Yellowness index	Sample 1	2.26	1.72	-23.9 [%]
	Sample 2	6.28	10.49	+67.0 [%]
Swelling degree	Sample 1	4.47	46.68	+944 [%]
	Sample 2	21.39	2.68	-87.5 [%]

## 2 Results and Discussions

Table.1 summarize the property changes before and after photo-aging in terms of multi-scale perspective. The CI is calculated as the ratio of the peak areas (C=O vibration and C–H vibration) in FTIR spectra, similar trends were shown for both samples, which indicates little difference in the chemical degradation (oxidation) rates between the two types.

Although the behaviour of E and the carbonyl index (CI) show common trends for both samples, the overall trends of yellowness index (YI) and swelling degree (Q) differ significantly between the pigmented and non-pigmented samples. The results reveal that changes in macroscopic properties may not necessarily correspond with the CI behaviour and that characteristic interfacial effects exist between the pigment and the binder. The different behaviour of YI and Q between the sample types might be attributed to the interfacial effect at pigment/binder interface based on the photo-catalytic effect from TiO<sub>2</sub> pigment.

The pore volume (related with Q value) of the binder was decreased, which might be associated with hardening and shrinkage as the result of extensive cross-linking formation in the aging behaviour of the non-pigmented sample. On the contrary, pore generation at the interfacial region at pigment/binder interface was implied in the pigmented coating.

## 3 Conclusions

Multi-scale analysis of photodegradation has been done for both pigmented (acrylic-urethane + TiO<sub>2</sub> pigment) and non-pigmented coating (only acrylic-urethane). We pointed out the difference of photodegradation scenarios between pigmented and non-pigmented coating and the effect of interface between pigment and binder.

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