

Cyclical Aging Tests in Latex Coating with TiO₂ Nanoparticles by UVb Radiation (Ujian Berkitar Penuaan dalam Salutan Lateks dengan Nanozarah TiO₂ oleh Sinaran UVb)

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ABSTRACT

This study evaluated the properties of adhesion, cracking, rusting, and accumulated irradiance on the surface of four vinyl acrylic resin coatings. QUV accelerated aging technique was applied. The coatings accumulated irradiance in cyclic form and was controlled by the tests of atmospheric temperature and relative humidity. A paper money currency validator counterfeit has been used because of its constant irradiance of 1,41 mW/cm²; a power of 9 W of UV radiation; 220 V, ranging an equipment temperature (OPALUX) between 40 °C and 60 °C. Irradiance has been measured by using the UV light meter equipment model YK-35UV (2 to 20 mW/cm²). Latex coatings embedded with TiO₂ nanoparticles and prepared in four different formulations with CaCO₃ plus Diatomite were applied on a surface area of 5.5 cm length times 1.5 cm width. The exposition time ranged from 56 to 500 h of irradiance at a period span of eight h each day. Coatings were altered on its properties of adhesion, elasticity and photooxidation on their surface.

Keywords: Aging technique; irradiance; latex coating; TiO₂ nanoparticle

ABSTRAK

Kajian ini menilai sifat lekatan, keretakan, pengkaratan dan sinaran yang diterima pada permukaan empat salutan resin akrilik vinil. Teknik penuaan dipercepatkan QUV telah digunakan. Salutan menerima sinaran dalam bentuk kitaran dan dikawal oleh ujian suhu atmosfera dan kelembapan relatif. Pengesanan mata wang kertas palsu telah digunakan kerana sinaran malar 1,41 mW/cm²; kuasa 9 W sinaran UV; 220 V, dengan julat suhu peralatan (OPALUX) antara 40 °C dan 60 °C. Sinaran telah diukur menggunakan model peralatan meter cahaya UV YK-35UV (2 hingga 20 mW/cm²). Salutan lateks yang dibenamkan dengan nanozarah TiO₂ dan disediakan dalam empat rumusan berbeza dengan CaCO₃ dan Diatomit telah digunakan pada kawasan permukaan 5.5 cm panjang × 1.5 cm lebar. Masa dedahan adalah antara 56 hingga 500 jam penyinaran pada jangka masa lapan jam setiap hari. Salutan telah diubah pada sifat lekatan, keanjalan dan fotooksidasi pada permukaannya.

Kata kunci: Nanozarah TiO₂; salutan lateks; sinaran; teknik penuaan

INTRODUCTION

Studies on cyclical aging tests in latex coating are relevant because many of them would have a relationship with the heating and cooling loads of buildings that are closely related to the absorption and reflection of solar radiation. These coatings that surround buildings can

greatly affect not only energy consumption, but also the use of new types of coatings that could help regulate the absorption of solar radiation (Zhang & Zhai 2019). Particle size must also be considered; that is, the higher the specific surface area, the greater the protection against UV rays. Coating wear is one of the most frequently reported

causes, therefore, it is considered important to study rusting resistance for coatings exposed to the elements (Fernández et al. 2020).

It is necessary to observe that the photo-degradation that occurs on a surface, where a color change occurs, is due to the action of UV light, the initial color of the coating, the exposure time, humidity, and temperature; additionally, the degree of environmental contamination (Varganici et al. 2020). In various investigations, changes in the mechanical properties of acrylic pseudo-paints containing nano TiO₂ are being considered, by applying photo-catalytic degradation under UV irradiation (Monfared & Jamshidi 2019). Nano-TiO₂ must be prepared in a dispersed form to maintain their properties since they tend to agglomerate, lose their physical properties, and are used to measure photocatalytic performance. To reduce air pollution, nano-TiO₂ showed secondary benefits, such as the increase in electricity generated by photovoltaic solar panels, solar irradiation of the surface, then generating benefits with a secondary effect, in increasing energy (Labordena et al. 2018).

Likewise, lignocellulosic materials also undergo degradation reactions as indicated by the light that is reflected during the modification of their mechanical and physicochemical properties, where an initial colour change, loss of gloss, roughness and cracking are observed. The solution nano-TiO₂ is important to be used in cold ceilings, in those ones with high reflectance and high emissivity; however, due to the high NIR reflection, some material used as cold roof coating showed high solar degradation. Visible reflection presents some restrictions that must be overcome, such as the application of a coated tile, with a new glass-ceramic coating, to improve, which is favorable for colored materials, the properties of solar reflection and reduction of thermal conductivity. The technology that hardens the coating is heat treatment through the polymerization of oligomers in ultraviolet light, although curing by ultraviolet UV radiation has found its wide application in industry (Akbulut et al. 2016).

Some studies have been conducted to evaluate the effect of accelerated aging by ultraviolet rays under controlled conditions on the propagation of surface cracking. These tests were developed in a UVB accelerated aging chamber, where the degree of cracking on the surface was observed (Andrés et al. 2013). In relation to other works, such as the poplar wood surface on which the artificial irradiation was exposed in a solar box, the measurement and control were carried out with a reflectance spectrometer (Agresti et al. 2013).

This research work showed the treatment of latex

coating with TiO₂ nanoparticles that were developed in four different formulas prepared with CaCO₃ and Diatomite. The accumulated irradiance ranged from 56 to 500 h. The focus of the research was centered on the application and evaluation of aging tests on the coating. It was observed how the coating altered its properties of adhesion, cracking, rusting and accumulated irradiance on the exposed surface.

MATERIALS AND METHODS

The preparation of latex coating film was carried out in three stages. In the first stage of dispersion, the ammoniacal solution, the antifoam and the dispersant were mixed for ten minutes, by stirring the mixture and, at an intermediate speed. In the second grinding stage, CaCO₃, TiO₂, cellulose, and AMP were added to the mixture; then, coverage and viscosity tests were performed. Finally, in the third stage of homogenization, resin was added; then, viscosity and thickness of the coating film were measured. Humidity of each stage was measured.

In a way, the latex coating film was composed of a vinyl acrylic resin made from TiO₂ nanoparticles and calcium carbonate or diatomite. Irradiance was measured with a model Opalux equipment (9 W and 220 V) and a UV Light meter equipment model YK-35UV (2 to 20 mW/cm²). The atmospheric control was carried out by means of Clock & Hydro-Thermometer brand Boeco Germany (+/- 0.01 °C). A 1600× digital microscope with USB input with aluminum stand, foil cutter with metal ruler and a Canon 35 Mbps imager with 57× zoom magnification was used.

Each treatment and Control Group were irradiated by using a QUV accelerated aging technique by 500 h on a latex coating surface area of 5.5 cm length times 1.5 cm width, and 1 cm thickness. Subsequently, adhesion, cracking, oxidation, and irradiance were measured and compared with ASTM standards D4541-02 (2002), D3359-09 (2009), G154-16 (2016), D661-93 (2011) galling tests and rusting grade tests according to ASTM D610-08 (2008) (Table 1).

The treatments were irradiated under usual environmental conditions of temperature and humidity. The experimental trials followed standard protocols: adhesion according to the ASTM standards D4541-02 (2002) and D3359-09 (2009); and QUV aging operation tests according to the standard ASTM G154-16 (2016), ASTM 661-93 (2011) galling tests and rusting grade tests according to ASTM D610-08 (2008).

TABLE 1. Control group and experimental treatment arrangement

Control Group	7% TiO ₂ (without nano particles) + 40% de CaCO ₃ (Micro powder)
Treatment 1	7% TiO ₂ (20 nm particles) + 40% CaCO ₃ (Micro powder)
Treatment 2	7% TiO ₂ (200 nm particles) + 40% CaCO ₃ (Micro powder)
Treatment 3	7% TiO ₂ (20 nm particles) + 40% Diatomite (Micro powder)
Treatment 4	7% TiO ₂ (200 nm particles) + 40% Diatomite (Micro powder)

RESULTS AND DISCUSSION

All cases of different mean comparison T-tests were statistically significant ($p < 0,05$) for environmental conditions of adhesion, cracking, oxidation, and irradiance properties.

TABLE 2. Percentage of relative humidity and temperature

per accumulated h of irradiance

H of irradiance	Environmental relative humidity (RH %) and temperature (°C)									
	6:00 a.m.		08:00 a.m.		10:00 a.m.		12:00 a.m.		2 p.m.	
	RH %	°C	RH %	°C	RH %	°C	RH %	°C	RH %	°C
56	75	23,3	71	27,4	55	29,6	44	32,4	36	34,6
120	74	23	68	27,1	51	30,1	42	32	37	34,1
180	76	21,6	71	22,6	53	27,8	46	29,8	43	32,2
240	76	20,9	68	23,9	55	26,6	49	28,4	45	31,2
300	79	20,1	70	23,2	58	25,1	49	27,7	52	29,1
360	79	19	68	21,5	58	24,5	49	26,8	52	28,3
420	82	17,9	83	18,9	70	21,7	58	24,4	53	25,8
480	81	18,4	72	20,4	67	22,4	58	25,7	53	26
500	83	18,2	80	19,1	70	20,6	61	23,3	54	24,7

No statistically significant difference was found among data of relative humidity nor temperatures. For this reason, the environmental factor did not influence the experiment (p -value $> 0,05$ Chi-squared). Table 2 constitutes a referent to set the environmental conditions under which experiment occurred.

As temperature was stable during the trials, it was found that accumulated irradiance quantity by treatments correlated with coating rehearsal (p -value $< 0,05$ Pearson, N). Table 3 shows the relation between

Irradiance and coating during the experiment. Also, Figure 1 shows that there is a positive directly proportional relation between irradiance and coating.

It was observed that the coating film after 500 h of irradiance with both formulae Treatment 1 and Treatment 4 showed greater loss of adhesion by almost 20%, while in both formulae Treatment 2 and Treatment 3 showed losses of 15% of adhesion. The control group showed 5 % removal. Temperature was almost constant. Cracking pattern was irregular for all treatments (Table 4).

TABLE 3. Record of accumulated irradiance, rehearsal test and temperature during the trials

Accumulated irradiance quantity (mW/cm ²)	Coating rehearsal test (h)	Temperature (°C) during trials
56.40	40	31.2
157.92	112	30
245.34	174	28.4
329.94	234	28.4
417.36	296	27
501.96	356	27.6
589.38	418	29
673.98	478	30.1
683.85	485	30.1
705.00	500	31.2

Table 3 shows how temperature remained almost constant (28 °C till 31 °C) despite of the accumulated irradiance quantity (W/cm²).

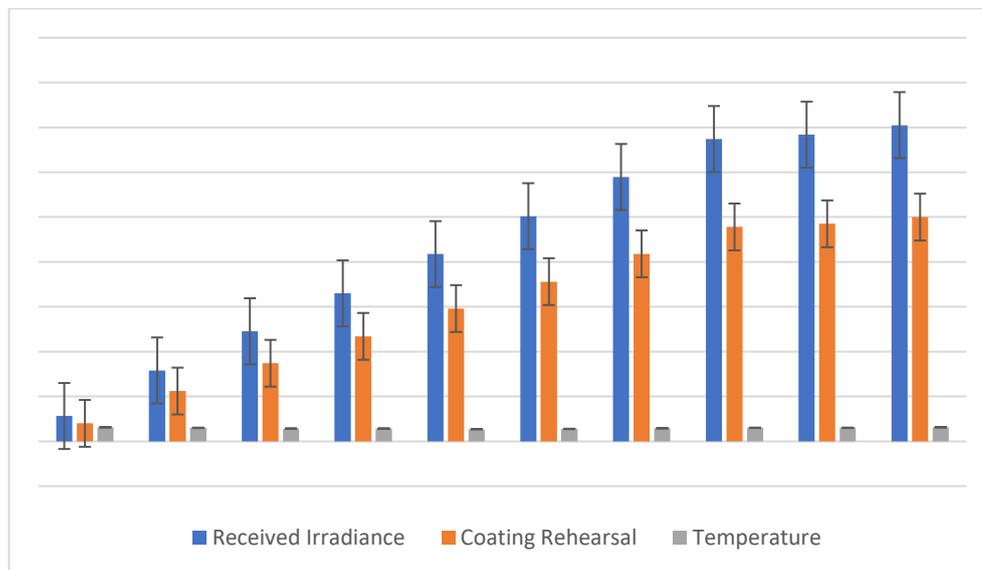


FIGURE 1. Accumulated irradiance, coating rehearsal test and temperature during the experiment

TABLE 4. Experimental results

Treatment	Average coating Temperature °C at zero h of accumulated irradiance	Average coating Temperature °C at 500 h of accumulated irradiance	Adhesion (% removal) till 500 h of accumulated irradiance	Cracking (Visual pattern)	Rusting (% oxidation) till 500 h of accumulated irradiance
Control	33,14	32,5	5	irregular	3
T1	35,84	33,84	20	irregular	33
T2	35,84	34,06	15	irregular	16
T3	33,96	31,96	15	irregular	3
T4	35,72	33,46	20	irregular	3

ADHESION RESULTS

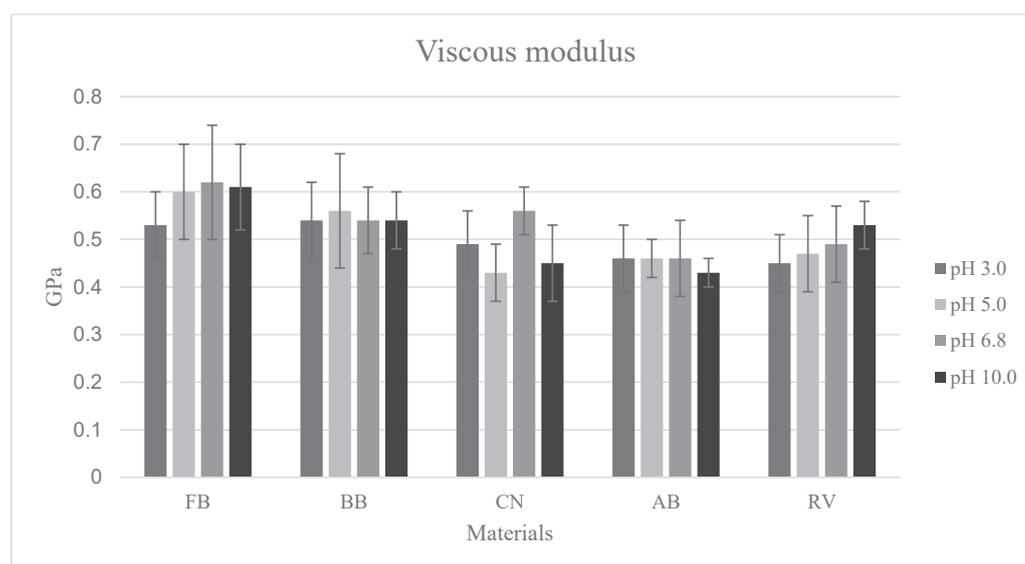


FIGURE 2. Adhesion results, the control group is the first one from left. A Digital Microscope 1600X Canon Vixia HF R600 32× Optical zoom was used for observations

At 500 h of irradiance, the Control Group showed 5% removal (i.e., 95% adhesion, first figure from left) whereas Treatment 1 removal was 20% (i.e., 80% adhesion); Treatment 2 equals 15% removal; Treatment 3 equals 15% removal and, finally Treatment 4 equals 20% removal, all cases according to ASTM D4541-02 (2002) (Figure 2).

The degree of attraction between the coating and the substrate in relation to the size of the TiO_2 nanoparticle did not influence similar results in formulations Treatment 1 to Treatment 4. These results demonstrated that the presence of nanoparticles did not favor adhesion on metallic surface of galvanized aluminum (according to ASTM D4541-02 (2002) and ASTM D3359-09 (2009) standards).

CRACKING RESULTS

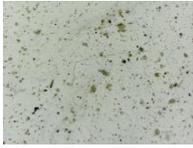
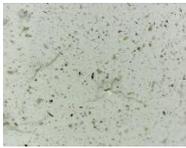
Treatment	Control	T1	T2	T3	T4
Cracking after 500 h irradiance					

FIGURE 3. Cracking. After 500 h of irradiance, the Control Group (first figure from left) showed a regular pattern of adhesion, whereas all other treatment patterns were irregular (ASTM D610). A Digital Microscope 1600X, Canon Vixia HF R600 32× Optical zoom was used for observations

The cracking results after five hundred (500) h of irradiance showed that the four formulations featured an irregular cracking as described in the ASTM D661-93 (2011), i.e., a vinyl acrylic base fully polymerized makes it less susceptible to cracking. The formation of rusting on the coating, as described in the ASTM D610-08 (2008) standard. Formula Treatment 1 presented a higher incidence of rusting formation, which covered

33% on its surface. Formula Treatment 2 showed a rusting formation of almost 15% on its surface, while both formulas Treatments 3 and 4 had a lower incidence of rusting formation at almost 3% each. It was observed that the formula Treatment 1 has a higher humidity, therefore it has a higher formation of rust as it condensed humidity on its surface thus preventing, at the same time, high adhesion (Figure 3).

DEGREE OF RUSTING RESULTS

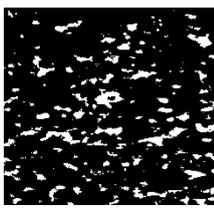
Treatment	Control	T1	T2	T3	T4
Rusting after 500 h irradiance	 3%	 33%	 16%	 3%	 3%

FIGURE 4. Degree of rusting for control group and treatments. A Digital Microscope 1600X, Canon Vixia HF R600 32× Optical zoom was used for observations

A visual pattern at 500 h of irradiance showed that there was 3% degree of rusting in Control Group (first figure from left), whereas the corresponding degree of rusting on treatments was: 33% for Treatment 1, 16%

for Treatment 2, 3% for Treatment 3 and, finally, 3% for Treatment 4, according to ASTM D610-08 (2008) (Figure 4).

The presence of an oxide reduction reaction on the surface of formula Treatment 1 is favorable, such as photodegradation for example, which occurred on one of the surfaces, according to the statement by Monfared and Jamshidi (2019). In formula Treatment 4 the temperature was kept constant over the coating in which it was exposed to five hundred (500) h of irradiance. The temperature of the coating of formula Treatment 4, was kept constant before being subjected to irradiance, then it was concluded that the coating formed an isothermal layer to ultraviolet radiation, this situation is related to the work of Zhang and Zhai (2019). In this way, the presence of TiO₂ nanoparticles contributes to the reduction of oxidation as does the low humidity in the coating prepared with diatomite.

CONCLUSIONS

The main attribute that nanoparticles have in the latex coating is to help a good distribution and homogenization after increasing its surface area, specifically titanium dioxide in the form of anatase (nanoparticles that cover smaller crystals). Nanoparticles tend to contribute to the retention of ultraviolet B radiation. In addition, nanoparticles - due to their sensitivity to visible light, size and anatase shape- contribute to the photocatalytic activity of TiO₂ (Titanium dioxide).

In this way, the degree of adhesion removal of the sample with code Treatment 4 was the one that presented the highest detachment (20%, ASTM D4541-02 (2002)). It was observed that flaws emerged irregularly and reached the substrate very superficially (ASTM D661-93 (2011)) during the cracking process of the surface layer. The highest degree of rusting formed was in Treatment 1 at 500 h of irradiance and considered more susceptible to form an oxide film on their surface (ASTM D610-08 (2008)).

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