



# Accelerated weathering of UV/EB curable clearcoats

C.S.B. Ruiz \*, L.D.B. Machado

*Institute for Energetic and Nuclear Researchers – IPEN/CNEN-SP, Av. Lineu Prestes, 2242, Cidade Universitária, 05508-000 São Paulo, Brasil*

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## Abstract

This study provides data regarding the behaviour of four UV- and EB-curable clearcoats – with or without light stabiliser additives – under accelerated weathering. The experimental data obtained from the weathered samples were evaluated and correlated to the formulation composition, type of radiation (UV or EB), radiation dose, and time in the ageing chamber. The results show that the EB-cured films have a better resistance to photoinduced weathering effects than do UV cured films. The UV/EB films with light stabilisers have shown greater stability than their counterparts with no additives. The ageing effects were evaluated by assessing parameters such as hardness, gloss, yellowness index, and changes in the Fourier transform infrared spectroscopy absorption bands.

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## 1. Introduction

Radiation curing is a field that has grown significantly as a direct result of its technological and environmental advantages. Due to its technological advancement this technology has become appropriate for use with materials used in external environments. An essential requirement for large-scale use of radiation-cured products is stability

regarding degradation caused by exposure to the elements. Some clear indications of degradation are yellowness, gloss reduction, hardness alteration, loss of adhesion to the substrate, increased permeability to moisture and oxygen, loss of flexibility and dimensional variations.

Studies in the literature have produced a variety of results and have shown correlations between ageing and various parameters responsible for degradation of radiation-cured coatings [1–6]. Some studies show that ultraviolet (UV)-cured coatings have less resistance when exposed to external environments than do films produced

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\* Corresponding author. Fax: +55 11 38169186.  
E-mail address: [csbruiz@ipen.br](mailto:csbruiz@ipen.br) (C.S.B. Ruiz).

through conventional curing processes such as those involving heat or catalysis. Degradation may be defined in terms of physical and chemical changes that occur during the exposure [7]. Some of the possible chemical origins of these changes are residual activity of functional groups, residual monomers, residual photoinitiators, areas of free-radical occlusion, products of photo fragmentation, peroxide decomposition, oxidation reactions, hydrolysis reactions, reactions induced by solar UV radiation, and heat-induced reactions. Notably among the physical causes are inadequate interfacial adhesion, differential cure profile, volume contraction during curing (internal stress), heat degradation, mechanical degradation (external stress and vibration), and moisture and O<sub>2</sub> migration. Some defects may be induced during the initiation process itself, whereas others may result from the rapid chemical process of polymerisation, and still others may subsequently develop from the interaction between the polymeric film and the environment [8].

In the current study, the behaviour of clearcoats cured with UV or EB radiation and submitted to weathering in terms of degree of cure and exposure time in a weather-ometer environmental chamber was evaluated. The parameters assessed were hardness, gloss and yellowness index, as well as infrared absorption bands correlated to the degradation of the films.

## 2. Experimental work

### 2.1. Clearcoats preparation

The clearcoats investigated (UV<sub>1</sub>, UV<sub>2</sub>, EB<sub>1</sub> and EB<sub>2</sub>) are composed of aliphatic urethane diac-

rylate resin (Ebecryl<sup>®</sup> 270) and 1,6 hexanediol diacrylate (HDDA) monomer (UCB do Brasil Ltda). A photoinitiator (2-hydroxy-2-methyl-phenyl-propan-1-one), Darocur<sup>®</sup> 1173, was added to the clearcoats to be cured by UV emission (UV<sub>1</sub> and UV<sub>2</sub>). Tinuvin<sup>®</sup> 400 (UV-absorber) and Tinuvin<sup>®</sup> 292 (hindered amine light stabiliser) HALS-type radicals scavenger (Ciba Especialidades Químicas Ltda) were added to the formulation named as UV<sub>2</sub> and EB<sub>2</sub>. Table 1 shows the composition of the clearcoat films: two (EB<sub>1</sub> and EB<sub>2</sub>) were formulated for EB curing, and two (UV<sub>1</sub> and UV<sub>2</sub>) for UV curing.

### 2.2. Preparation of films for accelerated ageing tests

Films, 50 µm thick, were placed on glass plates and irradiated by EB using a Dynamitron electron beam accelerator with energy of 1.5 MeV and 25 mA current (Radiation Dynamics, Edgewood, NY, USA). The EB<sub>1</sub> and EB<sub>2</sub> films were cured with 5, 10, 20, 40, 60 and 80 kGy doses of EB radiation, resulting in twelve samples. The UV<sub>1</sub> and UV<sub>2</sub> clearcoat films were cured with 50, 100, 200, 400, 600, 800 and 1000 mJ cm<sup>-2</sup> doses of radiation, using a Labcura<sup>™</sup>UV tunnel (Germetec UV & IR Technology Ltd., Rio de Janeiro, Brazil) and resulting in fourteen samples. The UV tunnel is composed of a medium pressure mercury lamp that operates at 300 W in<sup>-1</sup>. The UV radiation dose was monitored using a 390B Light Bug radiometer (International Light, Inc., Newburyport, MA, USA).

### 2.3. Accelerated ageing of cured films

Each set of samples was submitted to ageing exposure times of 100, 300, 500, 1000, 1500, 2000

Table 1  
Mass fraction (%) composition of EB<sub>1</sub>, EB<sub>2</sub>, UV<sub>1</sub> and UV<sub>2</sub> coatings

Components	Coating EB <sub>1</sub>	Coating EB <sub>2</sub>	Coating UV <sub>1</sub>	Coating UV <sub>2</sub>
Resin	64.9	63.9	63.0	62.0
Monomer HDDA	35.1	34.5	34.0	33.5
Photoinitiator	/	/	3.0	2.9
Tinuvin <sup>®</sup> 400	/	0.64	/	0.64
Tinuvin <sup>®</sup> 292	/	0.96	/	0.96

and 3000 h. The accelerated ageing tests were carried out using an Atlas 65-WRC-12 Weather-ometer (Atlas Electric Devices, Chicago, IL, USA), in compliance with the ASTM G-155 standard method test.

#### 2.4. Characterization of cured and aged films

The degree of cure of the clearcoat films was estimated through Differential Scanning Calorimetry (DSC), and the procedures were previously discussed [9,10].

The films submitted to accelerate ageing were characterized according to properties such as hardness, gloss and yellowness index. Photo-oxidation processes were monitored through Fourier transform infrared spectroscopy (FTIR) identification.

The FTIR analysis was carried out using a Nicolet 360 Avatar FTIR Spectrometer with an Attenuated Total Reflectance (ATR) accessory (Nicolet, Madison, WI, USA). The FTIR experiments were conducted with the aim of the attribution of absorption bands that are characteristic of the functional groups associated with the degradation process of cured film [11].

Tests to determine sample hardness were carried out using a BYK-Gardner pendulum hardness tester (BYK-Gardner, Geretsried, Germany), in compliance with the ASTM D-4366 standard test method. The glossmeter BYK Gardner Micro-Tri-Gloss was used to measure the gloss loss at an angle of 20° (ASTM D-523), as a function of

the ageing process. The yellowness index was determined using a Datacolor Spectraflash 600 colorimeter (Datacolor, Lawrenceville, NJ, USA) with d/8 geometry, 10° CIE standard viewer and D65 light source.

### 3. Results and discussion

#### 3.1. Cure degree

Table 2 presents the DSC the enthalpy data from uncured and partially cured samples, and also the calculated cure degree all samples. The influence of the coating composition on the cure degree was previously discussed [9,10].

#### 3.2. Hardness

Fig. 1 shows that hardness increases in parallel with increased radiation dose used in the curing up until it reaches a point at which it remains constant. The EB-cured films are harder than the UV-cured films. Fig. 2 shows the effects of ageing process on UV and EB-cured films with a similar degree of cure (95%), in terms of hardness. The EB<sub>2</sub> clearcoat cured films show smaller property variation than do the UV<sub>2</sub> clearcoat cured films. The EB-cured films are more resistant, in terms of hardness, than the UV-cured films, which begin to lose hardness after a 2000-h exposure time, compared to a 3000-h exposure time for the EB-cured films. Films with additives showed greater

Table 2  
Relative cure degree from uncured coatings and from samples previously cured at different UV or EB radiation doses

UV dose (mJcm <sup>-2</sup> )	UV <sub>1</sub>		UV <sub>2</sub>		EB dose (kGy)	EB <sub>1</sub>		EB <sub>2</sub>	
	$\Delta H^*$ (Jg <sup>-1</sup> )	Cure degree (%)	$\Delta H^*$ (Jg <sup>-1</sup> )	Cure degree (%)		$\Delta H^*$ (Jg <sup>-1</sup> )	Cure degree (%)	$\Delta H^*$ (Jg <sup>-1</sup> )	Cure degree (%)
0	271	Uncured	244	Uncured	0	275	Uncured	243	Uncured
50	31	88	62	75	2.5	27	90	25	90
100	26	90	26	89	5	21	92	19	92
200	18	93	22	91	10	16	94	13	95
400	16	94	19	92	20	12	95	13	95
600	15	94	16	93	40	10	96	12	95
800	12	95	11	95	60	11	96	11	96
1000	10	96	10	96	80	11	96	10	96

$\Delta H^*$ : residual enthalpy determined by DSC.

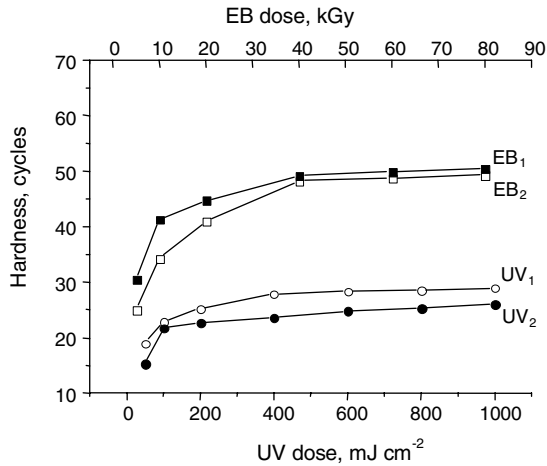


Fig. 1. Pendulum hardness of UV and EB cured films at different radiation doses.

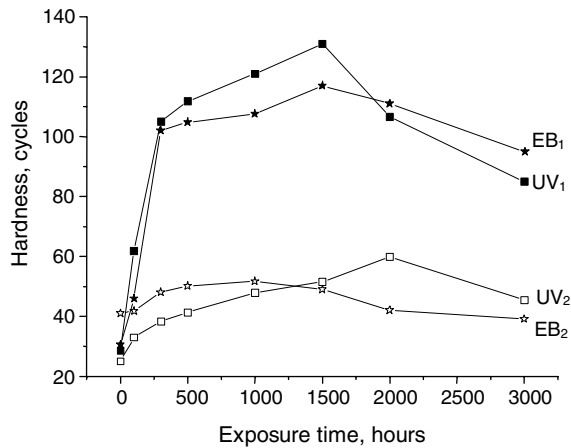


Fig. 2. Pendulum hardness of UV and EB cured films during weather-ometer exposure.

stability during accelerated ageing than did their counterparts with no additives. The samples of UV-cured films (UV<sub>1</sub>) as well as the samples of EB-cured films (EB<sub>1</sub>) showed an increase in hardness during the ageing process.

### 3.3. Gloss

Fig. 3 shows the results regarding gloss retention for UV and EB-cured films with a similar degree of cure (95%). The EB-cured films suffered a gloss loss

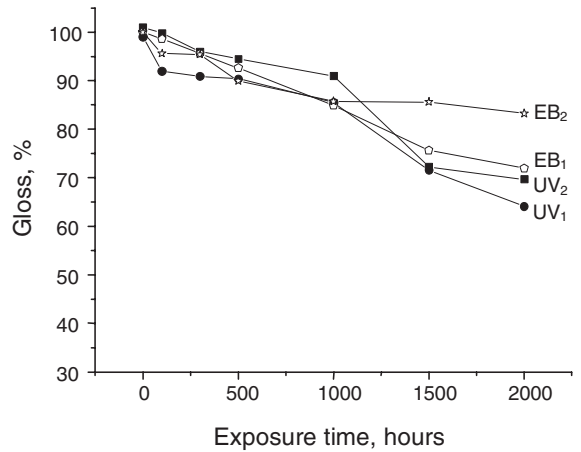


Fig. 3. Gloss retention of UV and EB cured films during weather-ometer exposure.

of approximately 25% (maximum gloss retention of 75%), compared with 35% for the UV-cured films. The presence of the UV absorber and of the HALS suppressor proved efficient in the case of the UV-cured films. In films cured using the UV<sub>1</sub> clearcoat, there was a glossiness increase in the samples cured with an UV radiation dose ranging from 50 to 200 mJ cm<sup>-2</sup>. At doses of 200 mJ cm<sup>-2</sup> and higher, there was still a tendency towards a glossiness increase, but with smaller gains than in the films cured with lower doses. In regard to the films that were cured using the UV<sub>2</sub> clearcoat, the glossiness

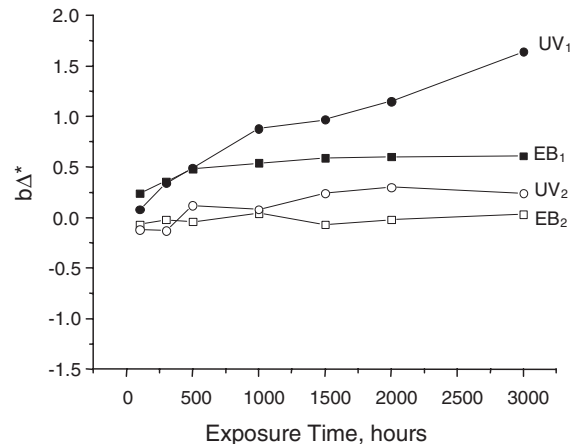


Fig. 4. Yellowing behaviour of UV and EB cured films during weather-ometer exposure.

increase occurs in parallel with the increase of the dose between 50 and 400  $\text{mJcm}^{-2}$ , after which these films show the same tendency as those with no additives. In EB-cured films, there was no tendency toward gloss values increasing in parallel with increased radiation dose within the range studied (5–80 kGy). In the EB<sub>1</sub> and EB<sub>2</sub> cured samples, there was a tendency toward decreased gloss values from 60 kGy on. This tendency may be due to the fact that the rate of the chain scission is higher than the rate of the polymerisation and

reticulation reaction, thereby impairing the formation of the polymeric system and interfering with the surface characteristics of the film. The EB-cured films retain glossiness more efficiently than do the UV-cured films.

### 3.4. Yellowness index (YI)

In the clearcoat film studied, the yellowness effect was minimised through the use of aliphatic urethane resin and HDDA monomer. The use of

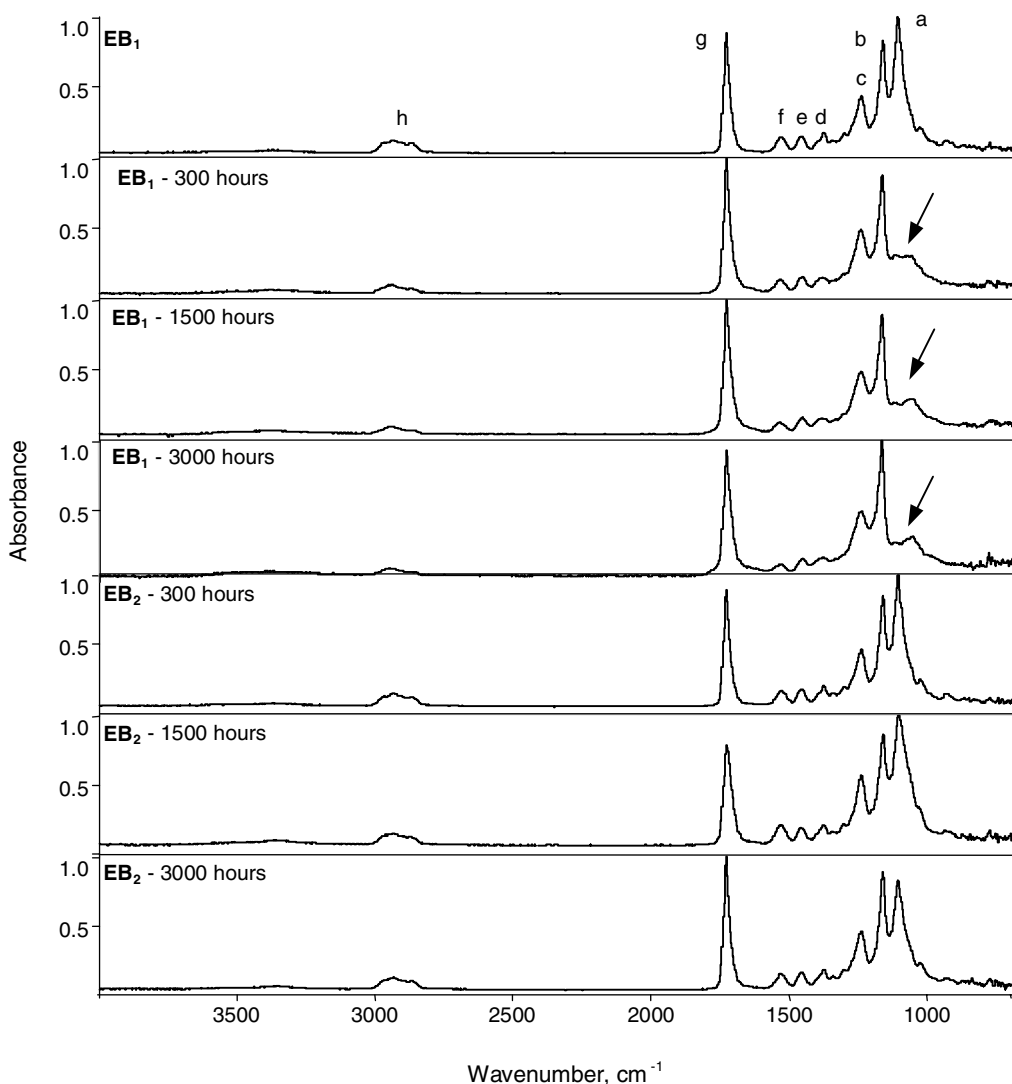


Fig. 5. Change in FTIR spectra of EB cured film during weather-ometer exposure.

the  $\alpha$ -hydroxyacetophenone-derived photoinitiator in the formulation also contributed to minimising yellowness. Fig. 4 shows the results of the yellowness index determination for UV- and EB-cured films with similar degrees of cure in terms of exposure time in weather-ometer. The results show that the UV-cured films have a stronger tendency to yellow than do the EB-cured films. This is precisely due to the absence of photoinitiator in the latter. The use of light stabilizers (UV absorber and HALS-radical scavenger) was efficient in controlling this tendency in both cases. The films cured using the EB<sub>2</sub> clearcoat show negative  $\Delta b^*$  values, which means that they do not have a tendency to yellow. Regarding the films cured using the UV<sub>1</sub> formulation, the  $\Delta b^*$  value of 0.5 is reached in all samples, at all doses of UV radiation applied during curing.

### 3.5. FTIR

Fig. 5 shows the FTIR/ATR spectra of the films generated from the EB<sub>1</sub> and EB<sub>2</sub> clearcoats, cured with electron beam radiation in order to illustrate the degradation process of the cured films during the exposure time in the weather-ometer chamber. The analysis of the results shows that all the absorption bands were altered, indicating degradation of the polymeric chain. The absorption band at 1106 cm<sup>-1</sup> showed the greatest height variation during the exposure to weathering, indicating scission of the ether linkages (C–O–C aliphatic antisymmetric stretch). After a 300-h exposure, this band was virtually absent from the spectra. Variations also occurred at 1375 cm<sup>-1</sup> (CH<sub>2</sub> in-plane deformation) and 1450 cm<sup>-1</sup> (CH<sub>2</sub> aliphatic in-plane deformation), although these were less intense. At 2930 cm<sup>-1</sup>, the band concerning to CH<sub>2</sub> stretching became 60% lower (in height) than that from the sample not exposed to weathering. Another sign of degradation appears in the absorption band at 1530 cm<sup>-1</sup>, which refers to the urethane linkage, indicating its rupture. The absorption band at 1725 cm<sup>-1</sup>, which refers to C=O stretching, reveals subtle exposure time-based band broadening. This might be attributable to the formation of carbonyl and carboxylic groups in the presence of oxygen. The results ob-

tained for the films cured using the EB<sub>2</sub> and UV<sub>2</sub> clearcoats showed the stabilizing effect of the additives. The exposure time-related height variation that was observed in the characteristic bands of the samples with additives (EB<sub>2</sub> and UV<sub>2</sub>) was irrelevant in comparison with that observed in the samples with no additives.

## 4. Conclusion

The choice of the resin, monomer and photoinitiator was planned in order to eliminate any influence of the parameters related to the chemical nature of on the variables studied. The light stabilising additives interfere with the UV curing process, thus reducing the degree of conversion at each level of dose considered. This fact is due to competition for the incident radiation between the UV absorber and the photoinitiator. In regard to hardness, there was a slight reduction in the values obtained for the films with additives. This is justified by the fact that this property relates more directly to a surface phenomenon than to the extent of cure throughout the layer. For the same degree of cure, the EB-cured films presented greater hardness than did their UV-cured counterparts. The ageing effect was more pronounced in the UV-cured films. This was observed by means of evaluating the various properties.

Increasing glossiness values related to degree of cure may be observed in films cured with UV at doses up to 400 mJ cm<sup>-2</sup>. The films irradiated with higher doses showed a tendency toward stabilisation of this property. However, the gloss retention during ageing is much more affected in UV-cured films. The gloss of the EB-cured film does not suffer alteration related to variations in dose. The tendency towards yellowness was higher in UV-cured films. Despite the use of aliphatic resin and monomer that are resistant to yellowness, the presence of photoinitiator in the composition of the clearcoat films probably induced colour development in the ageing process. The effect of the light stabilizers was more pronounced in the UV-cured films because these are more susceptible to photo degradation, probably due to the presence of residual chromophore groups.

The samples irradiated with the lowest and the highest levels of dose, within the ranges evaluated for the two types of radiation, were more influenced by the accelerated ageing process in the properties investigated.

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