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Influence of sample composition and processing parameters on the UV cure of clear coatings

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Abstract

Photocurable systems consist of functional macromolecules, which undergo polymerization and a photoinduced crosslinking reaction under UV irradiation. Radiation-curable coatings have gained importance because they are environmentally friendly and save more energy than conventional heat-curable processes. The performance of UV-curable coatings depends on their formulation and cure quality. The quality of UV radiation cure depends on lamp characteristics, photoinitiator (PI) content, film thickness, curing environment, substrate and temperature. The aim of this study was to evaluate the influence of coating thickness and UV radiation dose, as well as coating characteristics such as PI content and stabilizer additive composition, on the curing process.
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1. Introduction

The UV curing process converts a reactive liquid into a solid through polymerization and crosslinking reactions induced by UV radiation. Curable coatings consist of oligomers, monomers, photoinitiators, pigments and additives [1]. UV radiation absorbers and radical scavengers are used as additives to protective coatings for products submitted to external environments. These absorbers are modified aromatic systems, transparent in visible light and able to absorb UV radiation without forming reactive or radical species. The photoinitiator and the UV absorber, acting in different spectral windows, were included in the same formulation, which allowed the photoinitiator to be selectively activated. Radical scavengers are classified as "hindered amine light stabilizers" (HALS), which do not absorb significant UV radiation and prevent degradation of the cured film through catalytic conversion of radicals into stable compounds [2–4].

The extent of the cure is determined by factors including lamp characteristics, cure environment, coating thickness, substrate, temperature, UV radiation dose and coating formulation [5].

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Therefore, it was important to control each of the formulation components and, particularly, to know the nature of its reaction to the photochemical event. Some of these variables have been studied before [6,7], others are objects of this study. The effect of UV absorbers and HALS in the curing process, taking into account coating thickness and UV radiation dose, was studied.

Photocurable formulations have been evaluated by Abadie [2]. Differential photocalorimetry (photo-DSC) was the technique used to set the parameters for evaluating the UV curing. This technique also allowed for close monitoring of the curing process, approximating the actual industrial conditions under which coatings are cured by UV radiation.

2. Materials and methods

2.1. Materials and equipment

Two coatings (named A and B) were studied. The basic components of the coatings were: aliphatic urethane diacrylate resin (Ebecryl 270) and 1,6 hexanediol diacrylate monomer (HDODA) (both supplied by UCB do Brasil Ltda.); as well as the photoinitiator 2-hydroxy-2-methyl-1-phenyl-propane-1-one (Darocur 1173), the light stabilizer HALS (Tinuvin 292) and a UV radiation absorber (Tinuvin 400) (all supplied by Ciba Especialidades Químicas Ltda.). The compositions of coatings A and B are given in Table 1.

The coating formulations were cured at room temperature using a Labcure UV tunnel, manufactured by Germetec UV and IR Technology Ltd. This equipment consists of a medium-pressure mercury lamp and a conveyor belt with adjustable speed. The UV radiation doses were measured

with an IL 390B Light Bug radiometer from International Light Inc. The photo-DSC measurements were taken with a TA Instruments DPC 930/DSC 910, equipped with a medium-pressure mercury lamp (200 W in^{-1} and 80 mW cm^{-2}), using carbon-graphite pans and an empty carbon-graphite pan as a reference. The photo-DSC measurements were taken at 25 °C, in a nitrogen atmosphere, using a two-minute stabilization time and a three-minute exposure time, which were sufficient to achieve the total cure of the coatings samples under these measurement conditions.

2.2. Determination of cure degree

Samples of coatings A and B were irradiated in a UV tunnel. The cure degree was determined by means of the residual reaction heat of the undercured samples obtained with photo-DSC equipment. The percentage of cure degree was calculated using a relation formula (1). The values of total reaction heat (ΔH_{total}) for the coatings were obtained empirically using uncured coating samples. The values of residual reaction heat ($\Delta H_{residual}$) were calculated from the area of the photo-DSC exothermic peaks of the partially UV tunnel cured (undercured) samples. Some reaction enthalpies of well-known acrylate polymerization processes (77.9 kJ mol^{-1} per each double bond) [8] were not considered in this study because resins of industrial grade were used in coating formulations.

$$\text{Cure degree (\%)} = [1 - (\Delta H_{residual}/\Delta H_{total})] \times 100. \tag{1}$$

2.3. Effect of photoinitiator concentration

To determine the adequate concentration of photoinitiator, measurements of reaction enthalpies of 5 mg uncured samples of coating A with 0.5%, 1%, 2%, 3%, 4% or 5% photoinitiator were carried out in carbon-graphite pans using photo-DSC. The determined photoinitiator concentration was added to coating A and B formulations to study the effect of layer thickness and UV radiation dose on cure performance.

Table 1
Coating A and B composition (w/w %)

Components	Coating A	Coating B
Ebecryl 270	65.0	62.0
HDODA	35.0	33.5
Darocur 1173	0.5; 1; 2; 3; 4 or 5	2.9
Tinuvin 400	–	0.64
Tinuvin 292	–	0.96

2.4. Effect of layer thickness on cure degree of coating

For these evaluations, samples of coatings A and B were used with 3% photoinitiator. Samples of 2–10 mg were poured in graphite pans 5 mm in diameter and 3 mm in depth, resulting in layer thicknesses of 110–560 μm. Measurements of reaction heat, which is proportional to UV light penetration, were performed in photo-DSC. After the photo-DSC assay, layer thickness of each sample was measured in the center of the pan using a micrometer. Measurements were taken in dry layers (cured samples), despite the known shrinking effect due to curing reactions. These data were arbitrary because the effect of the meniscus was not considered.

2.5. UV radiation dose

Coatings A and B with 3% photoinitiator were poured in carbon-graphite pans until layers of about 200 μm were achieved. These samples were cured in a UV tunnel with doses of 50, 100, 200 and 600 mJ cm^{-2}. The residual curing reaction heat of each sample was determined in a photo-DSC. Cure degrees were calculated using relation (1).

3. Results and discussion

3.1. Effect of photoinitiator content in curing process performance

Table 2 shows the photo-DSC results obtained for Coating A. The curing heat values determined for uncured samples show that a 2% photoinitiator concentration is sufficient to achieve total cure of coatings in applied conditions of photo-DSC (exposure time and lamp characteristics). Heat reaction values of samples with 0.5% and 1.0% PI represent partial cure due to insufficient photoinitiator concentration. Induction time (related to the conversion of 1% of reactive species) decreases with the increase of PI in the range of 0.5–3.0%, remaining constant from 3.0% to 5.0%. Peak maximum values (time between the opening of the lamp shutter and the peak maximum point in photo-DSC curve when the reaction rate is the highest) have shown no variations with 3% or greater photoinitiator content. Thus, 3% was established as the most effective photoinitiator content for the subsequent studies.

Additionally, samples of approximately 220 μm in thickness were partially cured in a UV-tunnel with a 50 mJ cm^{-2} dose. The ΔH_{total} of 205 J g^{-1} (from uncured coating) was considered in the cure degree calculation. Cure degree increased in direct relation to increase in PI content. However, under the radiation dose applied, complete cure was not achieved (Table 2).

3.2. Effect of coating thickness

The photo-DSC measurements for coatings A and B at various layer thicknesses are presented in Table 3. Fig. 1 shows the photo-DSC curves of uncured samples of coatings A and B.

Even though peak height decreases as layer thickness increases, the area below the exothermic peak was similar among all samples of coating A. On the other hand, the area below the exothermic peaks from coating B samples decreased with an increase in layer thickness. This can be explained

Table 2
Photo-DSC results of uncured and partially UV-tunnel cured coating A samples – photoinitiator influence on curing process

PI (%)	Uncured samples			Partially UV-tunnel cured samples	
	ΔH_{total} (J g^{-1})	Induction time (s)	Peak maximum (s)	$\Delta H_{residual\ cure}$ (J g^{-1})	Cure degree (%)
0.5	178	2.4	6.8	112	45
1.0	190	2.3	6.2	91	56
2.0	203	1.5	5.0	84	59
3.0	205	1.0	4.4	45	78
4.0	205	1.2	4.3	36	82
5.0	204	1.1	4.4	22	89

Table 3
Photo-DSC data for uncured samples of coatings A and B with different layer thickness

Coating A				Coating B			
Coating thickness (µm)	ΔH_{total} (J g^{-1})	Induction time (s)	Peak maximum (s)	Coating thickness (µm)	ΔH_{total} (J g^{-1})	Induction time (s)	Peak maximum (s)
110	208	1.5	5.2	105	209	2.2	6.0
220	205	1.7	5.4	200	200	3.0	9.0
330	204	2.0	5.6	310	181	3.0	9.0
430	205	2.3	7.5	420	180	3.6	9.4
560	207	2.3	7.8	540	174	3.6	11.0

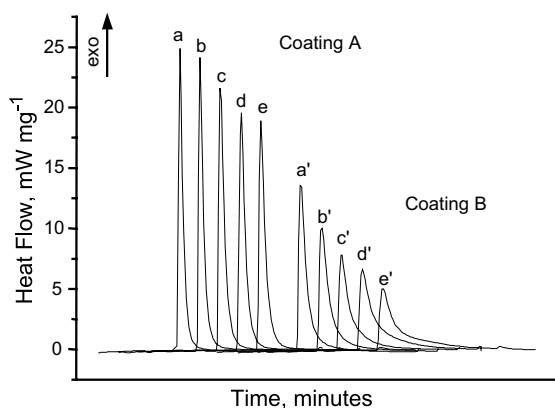Fig. 1. Photo-DSC curves – coating A and B thickness influence – (a) 110 µm, (b) 220 µm, (c) 330 µm, (d) 430 µm, (e) 560 µm and (a′) 105 µm, (b′) 200 µm, (c′) 310 µm, (d′) 420 µm, (e′) 540 µm.

by the presence of the UV absorber in the formulation for coating B. However, since reaction rates are higher in thinner samples, induction time and peak maximum both increase as coating thickness increases.

The Lambert–Beer law explains this effect by demonstrating that the rate of UV absorption in the layers nearer the surface is higher than in those in proximity to the coating/substrate interface. The thicker the layer, the greater the difference in the concentration of reactive species formed between the sample surface and the coating/substrate interface. This concentration influences the reaction rate.

3.3. Effect of the UV radiation dose applied

The effect of the UV radiation dose was evaluated for coatings A and B with samples of about 200 µm in thickness. The samples were pre-irradiated in a UV tunnel with doses in the range of 50–600 mJ cm^{-2}, then submitted to photo-DSC to evaluate the residual heat reaction. The results are given in Table 4. These data show the influence of stabilizer additives on the cure degree of the coating. When submitted to the same radiation dose, the samples with additives (coating B) present curing rates significantly lower than those obtained with the coating A samples. The UV absorber present in the formulation of coating B competes with the photoinitiator, partially absorbing the photons emitted by the lamp. This causes a reduction in the formation of free radicals and interferes with the curing process. However, the protection against solar radiation that this additive confers on the cured coating justifies its

Table 4
Cure degree evaluation of coatings A and B irradiated in UV tunnel

UV radiation dose (mJ cm^{-2})	Coating A		Coating B	
	$\Delta H_{residual}$ (J g^{-1})	Cure degree (%)	$\Delta H_{residual}$ (J g^{-1})	Cure degree (%)
0	205	Uncured	200	Uncured
50	45	78	151	24
100	22	89	147	26
200	13	94	39	80
600	9	96	21	89

incorporation. Increasing the UV radiation dose can minimize this effect.

4. Conclusion

The results show that coatings with 3% photoinitiator achieved better curing performance. In the samples studied, higher photoinitiator concentrations did not improve cure rate. In layer thicknesses greater than 200 μm, samples with UV absorber additives did not achieve curing reaction heat values comparable to those from thinner samples, even when submitted to high UV radiation doses.

Coatings A and B, even submitted to ±600 mJ cm^{-2} doses of UV radiation, were not capable of achieving complete cure. Coating B samples (with stabilizer additives) presented cure degrees lower than samples of Coating A (without additives) cured under the same conditions. Increasing the radiation dose can partially counterbalance the loss of conversion in coating B samples. However, doses higher than 200 mJ cm^{-2} did not significantly increase the extent of cure in coating A samples.

References

[1] S.P. Pappas (Ed.), UV Curing: Science and Technology, Vol. I, Technology Marketing Corporation, Connecticut, USA, 1980, 2nd printing.
[2] M.J.M. Abadie, Eur. Coating J. 11 (1991) 788.
[3] C. Lowe, P.K.T. Oldring, Test Methods for UV & EB Curable Systems, SITA Technology, London, UK, 1994.
[4] C.S.B. Ruiz, L.D.B. Machado, J.A. Vanin, J.E. Volponi, J. Therm. Anal. Calorimetry 67 (2) (2002) 335.
[5] C.G. Roffey, Photopolymerization of Surface Coatings, John Wiley & Sons Ltd., New York, 1982 (Chapter 4).
[6] C.S.B. Ruiz, L.D.B. Machado, J.E. Volponi, Third Brazilian Congress on Thermal Analysis and Calorimetry, Poços de Caldas-MG, 7–11 April 2002, Abstract, p. 142, J. Therm. Anal. Calorimetry, submitted for publication.
[7] C.S.B. Ruiz, L.D.B. Machado, VI National Meeting on Nuclear Application in 2002 INAC – International Nuclear Atlantic Conference, Rio de Janeiro, Brazil, 11–16 August 2002. Program & Abstracts VI ENAN, E11-532, Revista Brasileira de Pesquisa e Desenvolvimento, in press.
[8] D.C. Neckers, W. Jager, Chemistry & Technology of UV & EB Formulations for Coatings, Inks and Paints, Vol. VII, Photoinitiation for Polymerization: UV & EB at the Millenium, John Wiley & Sons, SITA Technology Limited, London, UK, 1998.