UV-dose indicator formulations as paint-on-photodetectors: A convenient and quantitative way to optimize the UV curing process

Katia Studer, Caroline Lordelot, Tunja Jung, Kurt Dietliker, Urs Lehmann, Peter Simmendinger, Eugene V. Sitzmann

Ciba, 205 S. James St., Newport DE 19804 USA

Abstract

A convenient and quantitative method that is useful for determining the effective UV exposure is described, which is based on new UV-dose indicator formulations. The UV dose indicators develop color as a function of the UV-dose applied during the curing process while simultaneously being cured. The method allows one to characterize the UV curing process over the whole surface of the coated article. It is particularly useful for three-dimensional coated objects. Color development with this system was found to be correlated to the applied UV light exposure as well as to the cure efficiency. The method offers to the end-user a way to forecast the coating properties, to optimize a radiation-cure process and to monitor the alteration of the energy source over time.

1. Introduction

Photocurable coatings are an important segment in the coating market [1,2], since they are fast curing and can be prepared at low temperatures. Photocuring involves exposure to light, to activate crosslinking and polymerization. This process results in a dry hard coating, which covers the surface of the object. The actual photocure efficiency depends on the amount of light absorbed [3]. The amount of light absorbed is a function of the light intensity, and measuring it at the surface of the object (especially as it relates to complex shapes) is the subject of this paper.

In the case of coatings that are applied onto a flat surface (i.e., for 2-D objects) the light intensity is generally measured by use of photodiodes. The geometries of 3-D coated objects, on the other hand, are more complex. Mapping the intensity of the incident actinic light over the entire surface topology is more complicated than compared to a 2-D surface. Thus, simple photodiode detectors are not easily placed in all the areas where the coating is applied. To measure the light intensity in those areas we need a different approach. One approach is to “paint on” a photo-detector [6]. At the heart of the paint-on detector is that it becomes colored after it is exposed to the light.

The specific system we chose to examine as the paint-on photodetector consisted of a photolatent colorant in a photo-curable resin. Several attractive features were engineered into this system, which include:

- The liquid paint detector is thermally stable

- It is easy to apply onto complex shaped parts
- The color that is developed after light exposure is easily detected visually, and
- The color is stable after photocuring is complete

2. Experimental

2.1. Paint-on-photodetector formulation

The composition of the paint-on-photo-detector consisted of a sprayable UV curable acrylate coating with added photolatent colorants. UV light exposure of this composition produces a strong red color [6].

2.2. Measurement of UV-light exposure

The paint-on detector system was applied onto white pre-coated aluminum panels by means of a 80 µm thick calibrated wire-wound bar coater to give a dry film thickness of about 40 µm. The UV-exposure was performed on an IST UV belt line equipped with two medium pressure mercury lamps (electric power of 40 or 80 $W.cm^{-1}$) at different belt speeds (ranged from 5 – 70 m/min) [6].

2.3. Characterization of color development

The selected colorant develops a red coloration, which was quantified by determining the CIE-Lab system a* value. The color evaluation was done using a using a Minolta spectrophotometer CM-3600d following ASTM E 308 methods [7]. A higher positive number for the a* value indicates a stronger red color.

A radiometer UV Power Map from EIT Inc. was used to measure UV-light on the conveyer belt. The diode detector is sensitive to the following regions: UVV (395-445nm), UVA (320-390nm), UVB (280-320nm), UVC (250-260nm).

The paint-on detector system consists of an acrylate resin. The percent conversion of the acrylate double bonds after light exposure was monitored at the coating surface *via* ATR-FTIR, using an Nicolet 380 FTIR Spectrophotometer and monitoring the absorbance change at 810 cm^{-1}[4].

Color development was further characterized spectroscopically by placing the paint-on detector resin onto a BaF_2 crystal, then measuring the absorption spectrum before and after UV light exposure.

3. Results and Discussion

3.1. Design of the paint-on photo-detector

The paint-on-photodetector needs to be sensitive to light that is typically used for UV curing and it also should track the photosensitivity of common photoinitiators used, such blends of alpha-hydroxy ketones and aryl phosphine oxide photoinitiators. It also should preferably have a viscosity such that it can be spray applied to the surface of the object.

The paint-on-photodetector system that was chosen contained a photolatent red colorant, since this color is strong and is easy to see visually. Other colors are possible.

We also adjusted the photosensitivity level so that it can be used in the low exposure range (less than 800 mJ/cm²). Other exposure ranges are also possible.

It is also possible to adjust the sensitivity to certain preferred spectral ranges. Namely, it is possible to adjust the paint-on-photodetector so that it is more (or less) sensitive to UVA or UVV spectral region of light [6].

3.2. Color Selection of the paint-on-photodetector

The color development after exposure to a Hg lamp output is shown in Figure 1. It was found that a strong absorption at approximately 550 nm developed after UV light exposure.

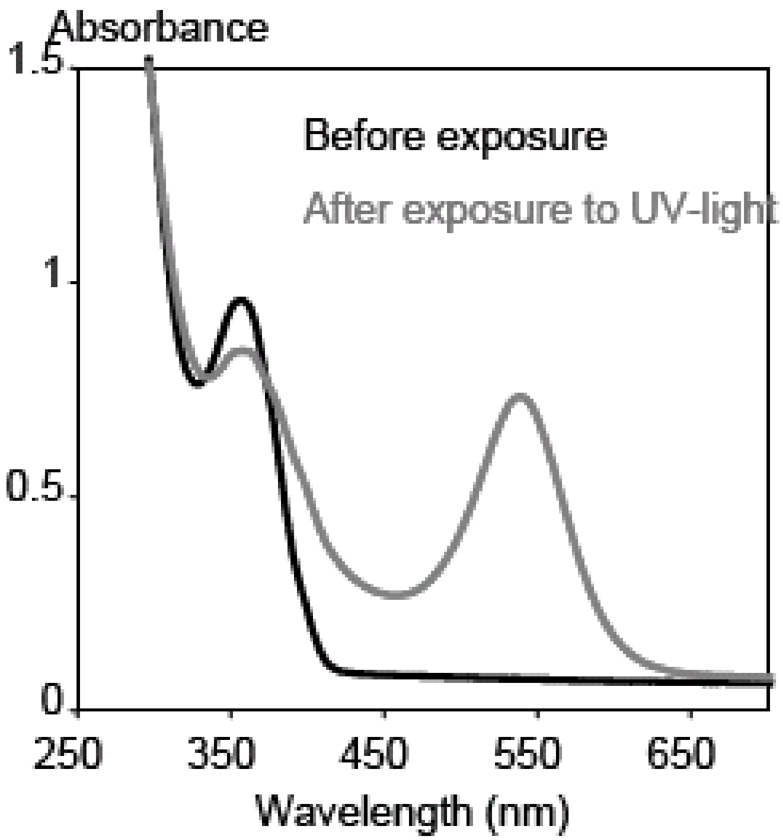

Figure 1. UV absorption spectra of the paint-on-photodetector, before and after a 150 mW.cm^{-2} UV-irradiance. 16 μm thick film

3.3. Setting the sensitivity range for the paint-on-photo-detector

It was found that the paint-on-detector was very sensitive to UV light, as shown in Figure 2. The practical limit for the paint-on-detector was between 40 to 800 mJ/cm². The lower practical limit was set by the sensitivity of measuring a* value. The upper limit was set by the chemistry of the paint. Namely, color is developed with increasing light exposure and reaches a maximum when the paint reaches its vitrification point (i.e., when it hardens) and becomes fully cured. This finding may be explained by the fact that the color forming process is based on a bimolecular reaction that is almost completely suppressed when diffusion becomes very low after vitrification. From FTIR analysis it was found that the %double bond conversion was 65% in the paint-on-photo-detector when maximum color was developed.

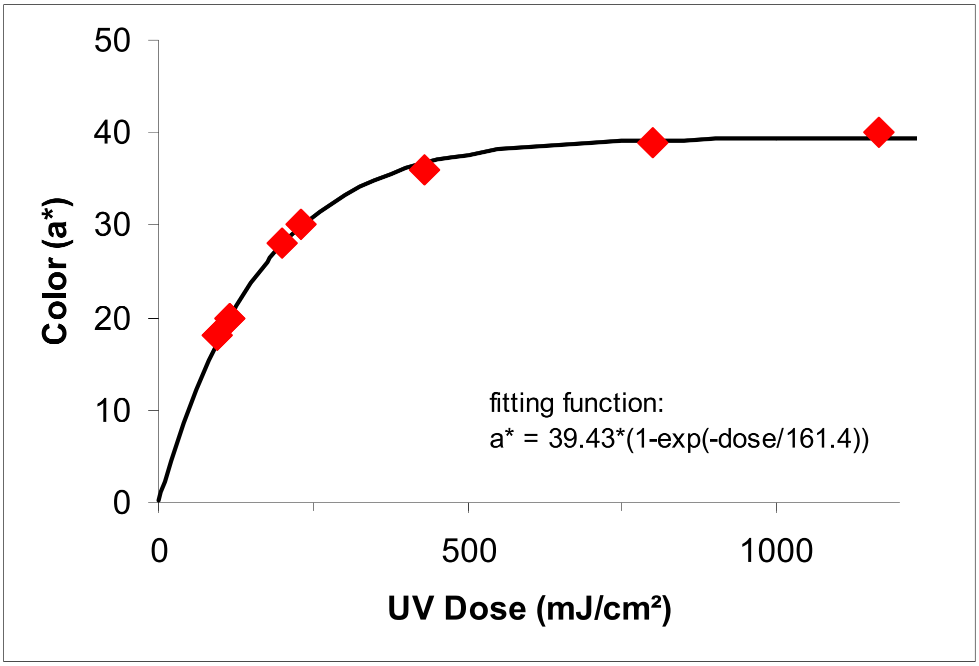

Figure 2. Calibration curve to relate color (a*) at the surface to UV light exposure

3.4. Thermal stability

Most commercial UV-dose indicating strips show a strong color dependency with respect to the irradiation temperature: this is a major problem when considering the heat generated by the lamp or other thermal effects which strongly differ from one to curing condition to another.

The influence of the film temperature during light exposure has been observed with the new paint-on-photodetector by curing it at different temperatures. The first film to be cured has been stored for 5 minutes at 140°C prior to light-irradiation and reached an a* value of 16 after a 150 $mJ.cm^{-2}$ light exposure. This value slightly increased to 18 when the experiment was repeated with the second sample at room temperature. This variation is in the tolerance range of a* measurement and visually no color difference could be observed. As a conclusion, these new UV-dose indicating systems are not temperature dependent within the accuracy of the intended application.

3.5. Dependence on film thickness

Obtaining homogeneous film thicknesses on large surfaces is quite challenging, whether one considers ink or coating applications. In the present case, the thickness is expected to affect color development as film absorption follows the Beer-Lambert law. A strong dependence of color formation on the film thickness would make the use of the UV dose indicator formulation difficult to use in practice for determining the applied dose or (i.e., UV light exposure).

To assess the color dependency as a function of this parameter, measurements were also done on film thicknesses comprised between 10 and 85 μm, and showed that within a region between 25 and 55 μm the color a* = 27 after an exposure to 200 $mJ.cm^{-2}$. The effect of film thickness is more pronounced when the thickness was less than 25 μm or when it was greater than 55 μm. In practice, it is recommended from time to time to verify the film thickness to confirm the result in order to assure that the UV exposure is determined in the range of linear response.

3.6. Demonstration on complex shapes

It is of interest to show how the paint-on-photo-detector can be used to characterize the UV curing process, especially of complex parts (like a car body). A demonstration was done using a car body shaped part and passing it under a mercury lamp. As shown in Figure 3, areas that show a strong red color are regions where the surface was exposed to high UV light exposure. The side panels and doors are regions where the surface received very low UV exposure and consequently the paint-on-photodetector shows low color.

Figure 3. Using of the paint-on-photodetector to characterize the UV light exposure of a part with complex geometries.

The paint-on-photodetector can be used to monitor the light curing process of coatings of complex 3-D shaped objects. The detailed knowledge of the UV exposure over the topology of the part (which the use of the paint-on-photodetector provides) permits us to set limits of the coatings' photoresponse and the type of lamps used to ensure good end properties of the coatings.

4. Conclusions

A convenient and sensitive method for determining the UV exposure at the surface of complex parts was described. The simple to use paint-on-photodetector can be used on complex shapes.

References

[1] C. Decker, Macromol. Rapid. Commun. 23 (2002) 1067
[2] C. Decker, Prog. Polym. Sci. 21 (1996) 593
[3] K. Studer, C. Decker, E. Beck, R. Schwalm, Prog Org. Coat. 48 (2003) 101
[4] C. Decker, K. Moussa, Makromol. Chem. 189 (1988) 2381
[5] C. Decker, K. Zahouily, D. Decker, T. Nguyen Thi Viet, Polymer 42 (2001) 7554
[6] K. Studer, C. Lordelot, T. Jung, K. Dietliker, U. Lehmann, P. Simmendinger, S. Villeneuve, Radtech Europe 2007, Vienna Nov. 23, 2007
[7] ASTM E308-06: Standard Practice for Computing the Colors of Objects by Using the CIE System.