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Accompanying of parameters of color, gloss and hardness on polymeric films coated with pigmented inks cured by different radiation doses of ultraviolet light

Marcelo Augusto Gonçalves Bardi*, Luci Diva Brocardo Machado

Comissão Nacional de Energia Nuclear, Instituto de Pesquisas Energéticas e Nucleares, CNEN-IPEN, Av. Prof. Lineu Prestes 2242, Cidade Universitária, 05508-000 São Paulo, Brazil

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In the search for alternatives to traditional paint systems solvent-based, the curing process of polymer coatings by ultraviolet light (UV) has been widely studied and discussed, especially because of their high content of solids and null emission of VOC. In UV-curing technology, organic solvents are replaced by reactive diluents, such as monomers. This paper aims to investigate variations on color, gloss and hardness of print inks cured by different UV radiation doses. The ratio pigment/clear coating was kept constant. The clear coating presented higher average values for König hardness than pigmented ones, indicating that UV-light absorption has been reduced by the presence of pigments. Besides, they have indicated a slight variation in function of cure degree for the studied radiation doses range. The gloss loss related to UV light exposition allows inferring that some degradation occurred at the surface of print ink films.

1. Introduction

UV light-induced cure of coatings has been developed during the last 30 years in a well-established technology for industrial applications (Bauer et al., 2007; Compston et al., 2008; Zhang et al., 2008). Photo-polymerizable formulations are now being increasingly used in various applications to achieve a fast hardening of protective and decorative coatings, printing inks, adhesives, varnishes and composites (Zhang et al., 2009).

The UV-curing of multifunctional monomers and oligomers is well known to guarantee the building up of polymeric thermoset matrices through a fast and environmental friendly process (Compston et al., 2008). Unlike the conventional solvent-based coatings, no weight loss is expected on photo-curable formulations (Bauer et al., 2007). Additionally, when the formulation is to be cured by UV light source, it is necessary to add photoinitiators, which absorb light and then generate free radicals responsible for inducing the chemical reaction between monomer and oligomer (Lee et al., 2006).

Due to the step-growth of polymerization mechanism, high molecular weight or highly crosslinked networks with substantial viscosities are not obtained until high conversion is reached, which is the case for conventional free radically curing systems (Nilsson et al., 2009). This allows a higher degree of curing to take place as a result of enhanced molecular mobility, resulting in a more homogeneous crosslinked network, as well as decreased material cure shrinkage after gelation, and improved substrate adhesion due to lower stress inside the cured film.

When manipulating UV coatings under different radiation doses, it is desirable to evaluate the color and gloss index, even though because these parameters are good indicators for the conversion degree of the samples. Gloss values range from 0 to 100. Nevertheless, to determine the exact combination of colors, coordinates of a three dimensional color space are assigned, as described by Chang and Lu (2010).

Additionally, hardness is also a property directly related to the efficiency of polymerization (Fedorov et al., 2007; Elsner et al., 2011). As described by Chan et al. (2009), the Persoz/König hardness is a measure of energy damping, heavily influenced by the energy loss, which occurs at mechanical transitions, i.e. glass transition.

According to Baikerikar et al. (2010), UV-cured coatings derived from 1,3/1,4-cyclohexanedimethanol diacrylate have significantly higher hardness as compared to other diacrylate monomers. This characteristic can be correlated to the higher crosslink density, as well as to the presence of cyclohexyl ring. On the other hand, the alkoxylated cyclohexanedimethanol diacrylates have significantly less hardness due to their higher molecular weight and the resulting lower crosslink density of cured coatings, as compared to 1,3/1,4-cyclohexanedimethanol diacrylate.

* Corresponding author. Tel.: +55 11 31339857; fax: +55 11 31339765.
E-mail addresses: magbardi@ipen.br (M.A.G. Bardi), lmachado@ipen.br (L.D.B. Machado).

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In this context, the aim of this paper is to evaluate color, gloss and hardness of print inks containing distinct pigments after irradiation at different doses of ultraviolet light.

2. Experimental

2.1. Materials

The following materials were applied for the preparation of the UV-curable clear formulation: Bisphenol A epoxy diacrylate (EBECRYL® 3720-TP25, Cytec Industries Inc.) diluted 25% by weight with tripropylene glycol diacrylate (TRPGDA, Cytec Industries Inc.); trimethylolpropane triacrylate (TMPTA, Cytec Industries Inc.); blend of photoinitiators 4,5/3,5/2,0 1-hydroxycyclohexyl phenyl ketone (Irgacure 184, Ciba-Geigy Co.)/2-hydroxy-2-methyl-1-[4-(1-methyl-vinyl) phenyl] propanone (Esacure KIP 150, Lamberti Co.)/ 2-dimethylamino-2-(4-methyl-benzyl)-1-(4-morpholin-4-yl-phenyl)-butan-1-one (Irgacure 379, Ciba Specialty Chemicals Inc.), respectively; talc (Nicron® 674, Luzenac America, Inc.); polydimethylsiloxane (Pure Silicone Fluid 100,000cSt, Clearco Products Co., Inc.); quinone derivative in propoxylated glycerol tri-acrylate (Irgastab® UV 22, Ciba Specialty Chemicals Inc.); polyethylene/ polytetrafluoroethylene wax (CeraSPERSE® 164, Shamrock Technology, Inc.).

In order to obtain colored print inks, pigments have been added to the clear coatings, such as the following: carbon black (Printex® 45 powder, Evonik Degussa GmbH), yellow pigment derived from diarylide m-xylidide (Irgalite® Yellow LBIW, Ciba Specialty Chemicals Inc.), blue pigment derived from phtalocyanine (Hostaperm Azul B2G 01-BR, Clariant Pigmentos e Aditivos Ltda.) and ruby pigment derived from monoazo (Rubide 4B, Hongyan Pigment Chemical Co., Ltd.). The ratio pigment/clear coating was kept constant (21/79 w/w) in order to investigate only the influence of each pigment under UV curing.

2.2. Films preparation and irradiation procedure

A manual applicator type Quick-Peek (Boanitec Indústria e Comércio Ltda., Cotia, SP, Brazil) was used to apply the colored print inks over glass. The thickness of the coating film was 7.0 μm ± 1.3 μm.

The coating formulations were cured at room temperature using a Labcure UV tunnel (Germetec UV and IR Technology Ltd., Rio de Janeiro, RJ, Brazil). This equipment consists of a medium-pressure mercury lamp and a conveyor belt with adjustable speed. The UV radiation doses were measured with an EIT UV PowerPuck radiometer from EIT Inc. (Sterling, VA, USA).

The coated glass plates were put on a conveyor able to move under UV light beam. The precise control of conveyor speed determined the radiation dose absorbed by the samples. The power of the lamp was fixed on 118 W cm^{-1}. This way, the doses of 150 mJ cm^{-2}, 220 mJ cm^{-2}, 310 mJ cm^{-2}, 550 mJ cm^{-2}, 850 mJ cm^{-2} and 1700 mJ cm^{-2} were applied to the samples.

2.3. Measurements

Color and gloss measurements were done using Byk-Gardner Spectro-Guide Sphere Gloss. D65/10° geometry was used, and data collection in the three different positions of the samples was performed. $L^*a^*b^*$ coordinates and gloss index are reported. The color difference between irradiated samples and non-irradiated ones was calculated according to the Equation:

$$\Delta E^*_{ab} = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (1)$$

The film hardness was measured using a Byk-Gardner König hardness tester. It was evaluated according to ASTM D4366 and reported in seconds.

3. Results and discussion

Tables 1–4 present the $L^*a^*b^*$ average color coordinates and average gloss index for all compositions studied, non-irradiated and irradiated at different UV radiation doses, and their respective standard deviation.

By analyzing data from Tables 1–4, it can be seen that each pigment is directly influenced by the UV radiation doses in a particular way, depending on the chemical family to which it belongs. According to Chang and Lu (2010), the index L^* is the lightness coordinate whose values range from 0 (black) to 100 (white); a^* is the red/green coordinate whose values range from −127 (pure green) to +127 (pure red); and b^* is the yellow/blue coordinate whose values range from −127 (pure blue) to +127 (pure yellow).

For yellow print ink (Table 1), it is observed a meaningful variation on color (ΔE^*) for compositions cured at 150 mJ cm^{-2}, suggesting that formulation is under-cured, indicated by a reduction at the b^* index. On the other hand, for the highest studied doses (850 and 1700 mJ cm^{-2}), an increase on the ΔE^* factor is also observed. The gloss index has also been reduced by those radiation doses, indicating a certain degree of degradation due to the exposition of the pigment to the UV light.

For the red print ink (Table 2), a different behavior is observed once higher values for L^* index are obtained for samples cured at 220 mJ cm^{-2} and 310 mJ cm^{-2}, indicating that compositions are cured. For the other radiation doses, it can be said that samples are either under cured (150 mJ cm^{-2}) or over-cured (doses higher that 310 mJ cm^{-2}). The gloss index corroborates this observation.

The compositions containing blue pigment (Table 3) do not show a clear tendency on the acquired data, only suggesting that the sample irradiated at 150 mJ cm^{-2} becomes under-cured. An observation at the gloss index reflects these comments, once its

Table 1
$L^*a^*b^*$ average color coordinates and average gloss index for yellow print ink, non-irradiated and irradiated at different UV radiation doses and their respective standard deviation.

Dose (mJ cm^{-2})	L^*	a^*	b^*	Gloss	ΔE^*
–	80.6 ± 0.2	6.2 ± 0.5	81.8 ± 0.4	16.6 ± 1.4	–
150	81.7 ± 0.1	−0.2 ± 0.02	67.5 ± 0.3	16.1 ± 0.3	15.7
220	80.7 ± 0.2	8.2 ± 0.4	77.8 ± 0.7	19.2 ± 0.9	4.5
310	81.6 ± 0.3	6.5 ± 0.2	77.1 ± 0.7	19.1 ± 1.6	4.8
550	82.2 ± 0.4	3.6 ± 0.3	79.0 ± 0.4	21.6 ± 0.3	3.0
850	78.9 ± 0.2	11.5 ± 0.1	78.9 ± 0.3	16.3 ± 0.6	6.3
1700	79.1 ± 1.0	8.0 ± 0.5	72.4 ± 2.0	15.1 ± 1.2	9.7

Table 2
$L^*a^*b^*$ average color coordinates and average gloss index for red print ink, non-irradiated and irradiated at different UV radiation doses and their respective standard deviation.

Dose (mJ cm^{-2})	L^*	a^*	b^*	Gloss	ΔE^*
–	41.9 ± 0.4	45.6 ± 0.6	15.3 ± 0.9	13.2 ± 0.5	–
150	42.2 ± 0.1	46.5 ± 0.1	20.1 ± 0.5	18.2 ± 0.9	4.9
220	46.3 ± 0.2	50.1 ± 0.4	10.0 ± 0.5	22.1 ± 0.6	8.2
310	47.4 ± 0.3	53.0 ± 0.2	5.2 ± 0.3	27.2 ± 1.1	13.7
550	43.5 ± 0.2	49.3 ± 0.3	16.1 ± 0.5	24.1 ± 0.3	4.1
850	44.4 ± 0.1	48.5 ± 0.3	13.5 ± 0.2	18.1 ± 0.6	4.2
1700	42.4 ± 0.4	46.6 ± 0.5	17.2 ± 1.3	11.4 ± 1.0	2.2

Table 3
$L^*a^*b^*$ average color coordinates and average gloss index for blue print ink, non-irradiated and irradiated at different UV radiation doses and their respective standard deviation.

Dose (mJ cm^{-2})	L^*	a^*	b^*	Gloss	ΔE^*
–	44.6 ± 0.2	−14.6 ± 0.3	−42.2 ± 0.2	21.2 ± 1.0	–
150	46.5 ± 0.8	−16.5 ± 0.4	−42.4 ± 0.8	32.2 ± 2.5	2.7
220	34.7 ± 0.03	−2.1 ± 0.1	−32.7 ± 0.2	8.1 ± 0.2	18.6
310	39.1 ± 0.2	−7.3 ± 0.3	−38.1 ± 0.4	16.6 ± 1.3	10.0
550	40.5 ± 0.2	−9.4 ± 0.5	−40.1 ± 0.2	20.3 ± 0.8	6.9
850	36.8 ± 0.8	−4.9 ± 0.2	−36.1 ± 1.0	15.6 ± 0.4	13.9
1700	38.7 ± 0.3	−7.9 ± 0.2	−39.4 ± 0.2	12.7 ± 0.7	9.3

Table 4
$L^*a^*b^*$ average color coordinates and average gloss index for black print ink, non-irradiated and irradiated at different UV radiation doses and their respective standard deviation.

Dose (mJ cm^{-2})	L^*	a^*	b^*	Gloss	ΔE^*
–	27.1 ± 1.7	1.6 ± 0.2	−0.9 ± 0.6	19.4 ± 2.9	–
150	25.0 ± 0.05	1.6 ± 0.1	−0.4 ± 0.03	11.4 ± 1.0	2.1
220	25.6 ± 0.1	1.8 ± 0.03	0.3 ± 0.03	18.4 ± 0.6	1.9
310	25.5 ± 1.1	1.7 ± 0.02	0.2 ± 0.02	13.8 ± 1.0	1.9
550	25.7 ± 0.03	1.7 ± 0.01	0.3 ± 0.03	13.1 ± 0.1	1.8
850	25.2 ± 0.3	1.8 ± 0.1	−0.6 ± 0.04	9.5 ± 0.8	1.9
1700	27.0 ± 0.3	2.1 ± 0.02	−0.5 ± 0.03	7.5 ± 0.1	0.6

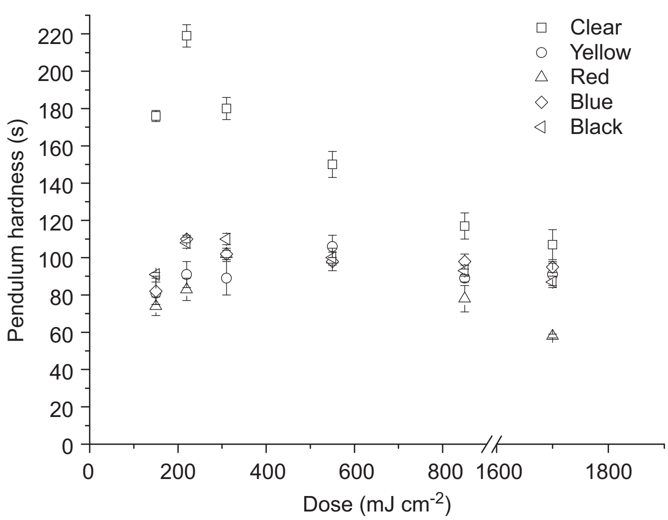

Fig. 1. Average König hardness for compositions irradiated at different UV radiation doses, and their respective standard deviation.

average values have all reduced when radiation doses superior to 150 mJ cm^{-2} have been applied on the sample.

When it comes to black print ink (Table 4), a meaningful difference on the color of the irradiated samples is not observed when compared to the nonirradiated one. By the analysis of the gloss index, a reduction is noted on its average values for all irradiated samples, which indicates a certain curing degree, but which has not been so satisfactory when compared to the samples of other colors.

Fig. 1 presents the average König hardness values for all compositions studied, non-irradiated and irradiated at different UV radiation doses, and their respective standard deviation.

The analysis of Fig. 1 allows observing the influence of studied pigments on hardness of UV-cured compositions. Bombard et al. (2008) alert that some properties depend on the kind of pigment contained in the coating formulation, as they depend on how deep the radiation penetrates the coating. Additionally, the presence of pigment in photopolymerizable formulation results by the decrease of monomer conversion and polymerization rate in comparison with the clear coating (Macarie and Ilia, 2007). Thus,causes a reduction on the hardness values of the pigmented coatings.

Pigments promote either scattering or absorption of UV photons and then the curing degree tends to have different behavior than the one for clear coating composition. Red and yellow formulations reached lower hardness values than blue and black ones, which is corroborated by Macarie and Ilia (2007).

As also corroborated by Ruiz et al. (2002), when studied coating formulations without pigments, the conversion degree for samples cured at UV radiation doses from 400 mJ cm^{-2} to 1200 mJ cm^{-2} reached a value, whose variation is not meaningful, but there is a residual non-reacted fraction that cannot be modified by increasing the radiation doses.

4. Conclusion

Gloss and hardness properties are directly influenced by the different classes of pigments incorporated to the formulations. The clear coating presented higher average values for König hardness than pigmented ones, indicating that UV-light absorption has been reduced by the presence of pigments. Besides, color and gloss indices from all formulations have indicated a slight variation in function of cure degree for the studied doses range. Over-cured samples have shown yellowness and reduction of gloss indicating degradation on the surface of the product.

This study can be useful on establishing curing conditions once that modern processes can use different radiation doses for each print ink layer depending on the pigment present on the formulation.

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