Photoinitiator Effect on Depth of Cure in Visible Light Cure Polymerization

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Abstract

The choice of photoinitiator (PI) is an important factor in the polymerization characteristics of light cure materials. This study investigated the influence of PI type and concentration on the surface tackiness and depth of cure (DOC) of experimental light cure acrylate formulations with several UV/visible photoinitiators. The chosen UV/visible photoinitiators include Type I PI phosphine oxide derivatives and Type II PI thioxanthone derivatives. Surface tackiness and DOC were also studied using two different radiation intensities emitted by LED 405nm curing lights**.** A Design of Experiment (DOE) using Response Surface Methodology (RSM) was used to optimize thioxanthone and amine synergist concentrations for the most desired surface curing and DOC. The correlations of PI type and concentration with DOC help light cure material formulation to achieve a tacky free surface and suitable depth of cure, which are important in many adhesive applications.

Introduction

UV-curable adhesives are single-part products which can be cured rapidly and by demands when exposed to UV-light to form a high-strength material. Different UV adhesive products have been designed with different cure speeds and cure wavelengths. Cured adhesive properties include adhesion to substrates, surface tackiness, depth of cure, mechanical properties such as hardness and tensile strength, tensile elongation and modulus. Several factors affect light curing adhesive performances: the material's composition, the choice of photoinitiators and the concentration of the initiators, temperature, the peak wavelengths and bandwidth of the curing light, the intensity of the light and the irradiation time.[1-3]

Depth of cure (DOC) is an important property to evaluate adhesive curing performances and guideline to applications. There are some literature studying the parameters affecting DOC of dental composites, but not many in adhesive areas. Parameters affecting DOC include: 1) Light intensity: DOC in general increases with increasing intensity of the curing light. 2) Type of light: UV light with wavelength below 365 nm will cure the surface extremely fast and quickly vitrifying the surface, blocking the UV light and preventing the material below from curing. UV to visible light with wavelength above 385 nm or higher cure the material more uniformly and allow the UV light to penetrate and cure adhesives in thicker sections. The closer the wavelength towards visible range the easier it will be to cure through larger gaps. 3) material opacity and color: increasing opacity and color will decrease DOC, 4) Type of PI: Generally there are two types of PIs. Norrish Type I PI produces free radicals by PI cleavage. Type II PI generates free radicals with PI abstracting hydrogen from a co-initiator (amine synergist).[4-5] PI should be chosen dependent on the UV lamp with a spectral output which peaks in the optimal range for the adhesive cure. 5) Concentration of PI: it is PI dependent. It has been observed that as the PI concentration is increased, the cure depth initially increases but then starts to decrease after reaching an optimal PI concentration.

Surface tackiness caused by atmospheric oxygen is also important for light cure acrylate adhesives. All the parameters affecting the DOC will influence surface tackiness of the cured adhesive.

In this study, different visible photoinitiators (absorbs at wavelength >400nm) were studied to understand the effect of PI type and concentration on the surface tackiness and DOC. Many methods, such as hardness tests, interaction with color dyes, translucency changes, double-bond conversion, NM tactile tests, penetration tests and scraping tests, have been used to measure the DOC. In this paper, DOC was measured using a scraping method adapted from ISO 4049. [6] There are many surface tackiness tests, and an easy qualitative way is to dust with silicon carbide or talcum powder on cured surface and then remove the powder by gentle rubbing or brushing. [7]

Materials

Table 1 is the list of the visible photoinitiators and amine synergists used in this study. Table 2 is a general formula containing different visible PI with or without amine synergists for this study.

Table 1 List of the visible photoinitiators and amine synergists

PI	Supplier	Amine synergist	Supplier
Omnirad 819	IGM	Visiomer DMAPMA	Evonik
Omnirad TPO	IGM		
Omnirad L-TPO	IGM		
Genocure ITX	Rahn		
Genopol TX-2	Rahn		
Omnipol TX	Rahn		

Table 2 General light cure formulas

Component	Wt%
Urethane acrylate	45-55
Acrylate monomer	40-50
Visible PI	0.1-3
Amine synergist	0-5

Sample Preparation and Testing Methods

Photoinitiator UV/Visible absorbance spectrum: UV/Visible spectrum of the PIs in Table 1 was acquired using ARM-1061 UV/Visible Spectrophotometric with each PI at three different concentrations 0.01, 0.1 and 1 wt% in acetonitrile.

DOC test: Each sample based on the formulation in Table 2 was put into a plastic cylinder with 13mm height and 6 mm diameter. The surface was flattened using a spatula and was cured using LED

405nm flood lamps. The sample was removed from cylinder. The bottom soft part was removed. The DOC is the height of the cured solid.

Surface tackiness test: Each sample in Table 2 was applied on a glass slide to form a thin layer and then was cured using LED 405nm flood lamps. Silicon carbide particles was applied on cured resin surface and brushed lightly to remove the powder. It is considered tacky if the black particles remain, and tacky free if no visible remaining black particles.

LED 405nm light intensity and dosage: measured by LED visible UVV radiometer (Item # 1265282, Henkel ID: 5995 , S/N UVV0059). Table 3 is the summary of LED 405nm flood light intensity and dosage with two curing time. These are the curing conditions used for all the testing unless specified otherwise.

Table 3 LED 405nm flood lamp light intensity and dosage with two curing time

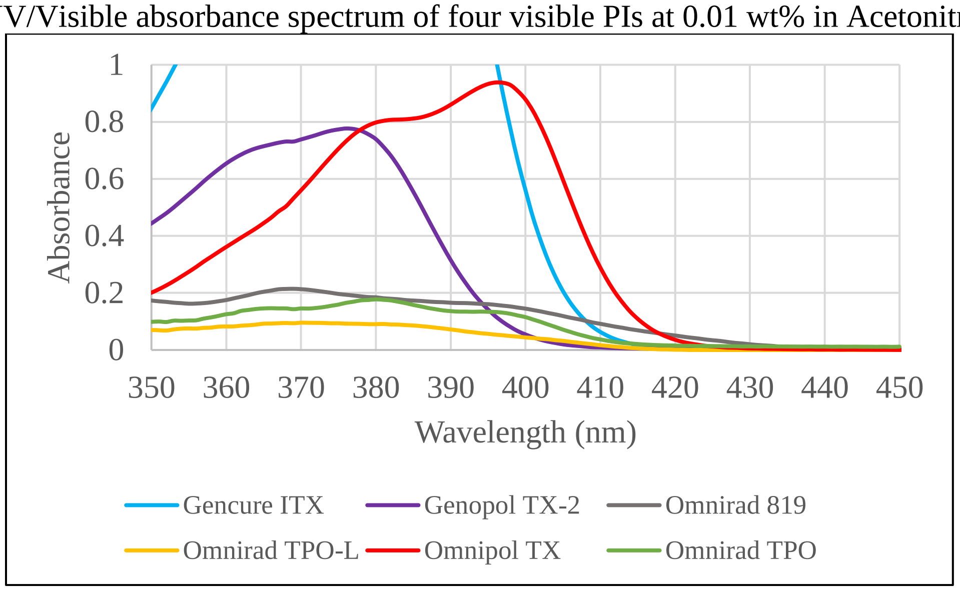
LED 405nm Light intensity (W/cm^2)	Curing time (sec)	Dosage (J/cm^2)
1.50	10	13.7
1.53	5	6.73

Results and Discussions

UV/Visible analysis of various visible photoinitiators

UV/Visible absorbance spectra of the six photoinitiators: Three Type I phosphine oxide based visible PIs Omnirad 819, TPO and L-TPO, one monomeric Type II PI thioxanthone Genocure ITX and two polymeric Type II PI thioxanthone derivatives Genopol TX-2 and Omnipol TX were studied. Figure 1 is the PI absorbance spectra at wavelength 350-450 nm with 0.01 wt% of PI in acetonitrile solution. These PIs all have absorbance at visible range 400-410nm.

Figure 1 UV/Visible absorbance spectrum of four visible PIs at 0.01 wt% in Acetonitrile



The absorbance values at 405nm of each PI at concentration of 0.01, 0.1 and 1 wt% are listed in Table 4. The absorbance increases with concentration, but not linearly as Beer's law is not valid at higher concentrations.[8] Among the six visible PIs tested, the absorbance of these PIs at 405nm at 0.01% level has the order of: Omnipol TX>Genocure ITX>Omnirad 819>Omnirad TPO >Omnirad TPO-L>Genopol TX-2. The trend is similar with other concentrations, but to a different extent. The absorbance at UV range 370-380nm is bigger than the absorbance in the visible range.

Table 4 PI 405nm absorbance at different concentrations

PI	PI concentration in acetonitrile		
	0.01%	0.10%	1.00%
Omnipol TX	0.6	2.82	3.27
Genocure ITX	0.21	1.78	2.87
Omnirad 819	0.12	1.21	3.3
Omnirad TPO	0.07	0.56	2.68
Omnirad TPO-L	0.03	0.33	2.32
Genopol TX-2	0.02	0.18	1.73

The PI absorbance is directly related to its reactivity at the wavelength light is emitted and will impact the DOC and surface tackiness tested in this study.

DOC and surface tackiness study

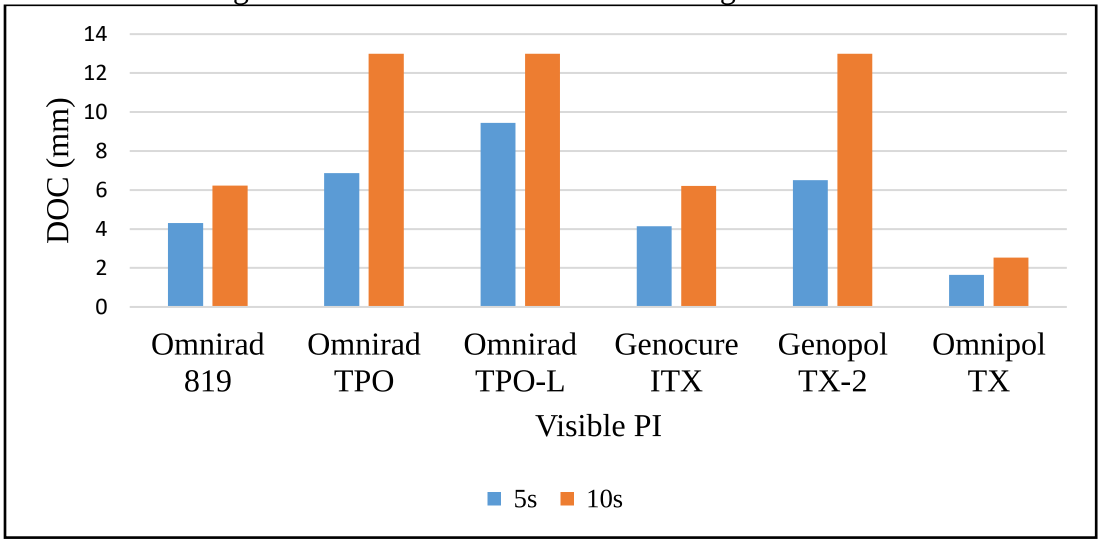
DOC and surface tackiness of the formulas containing different PIs

Three Type I phosphine oxide based visible PIs Omnirad 819, TPO and L-TPO, one monomeric Type II PI thioxanthone Genocure ITX (ITX) and three polymeric Type II PI thioxanthone derivatives were studied using the same curing condition. The PI loading for this testing was 1%. For Type II PIs, 2% of amine synergist Visiomer DMAPMA (DMAPMA) was added. The samples 1.1-1.5 were cured using LED 405nm. Table 5 is the summary of the DOC and surface tackiness testing results of the formulas containing different PIs with 5s and 10s curing time, respectively. Figure 2 is a graph showing the correlation of DOC and PI type.

Table 5 Summary of the DOC and surface tackiness of the formulas containing different PIs

Sample	PI	5 s cure		10s cure	
		DOC (mm)	Surface tackiness	DOC (mm)	Surface tackiness
1.1	Omnirad 819	4.30	No	6.22	No
1.2	Omnirad TPO	6.86	Yes	13.00	Yes
1.3	Omnirad L-TPO	9.45	Yes	13.00	Yes
1.4	Genocure ITX	4.15	No	6.21	No
1.5	Genopol TX-2	6.50	Yes	13.00	Yes
1.6	Omnipol TX	1.65	No	2.53	No

Figure 2 DOC of the formulas containing different PIs



Results in Table 5 and Figure 2 showed that DOC is dependent on the PI used and curing time. DOC increases with curing time for all the PIs. For the three Type I Omnirad 819, TPO and L-TPO, it is demonstrated that the absorbance value or reactivity at 405nm is in the order of 819>TPO>L-TPO. For the three Type II PIs, ITX and TX-2, the absorbance or the reactivity at 405nm is in the order of Omnipol TX>Genocure TX>Genopol TX-2. However, DOC increases with decreasing reactivity at 405nm. The results are consistent with both 5s and 10s curing. In this situation, lower PI reactivity favors DOC.

On the contrary, surface tackiness tests of the formulations with different PIs showed good correlation of free surface tackiness with PI reactivity. The data showed surface tacky free of the formulas with high reactivity PIs Omnirad 819, Genocure ITX and Omnipol TX. Other PIs with lower reactivity Omnirad TPO, L-TPO and Genopol TX-2 showed surface tackiness after both 5s and 10s curing although DOC is relatively higher.

DOC and surface tackiness of formulas containing PI with different concentrations

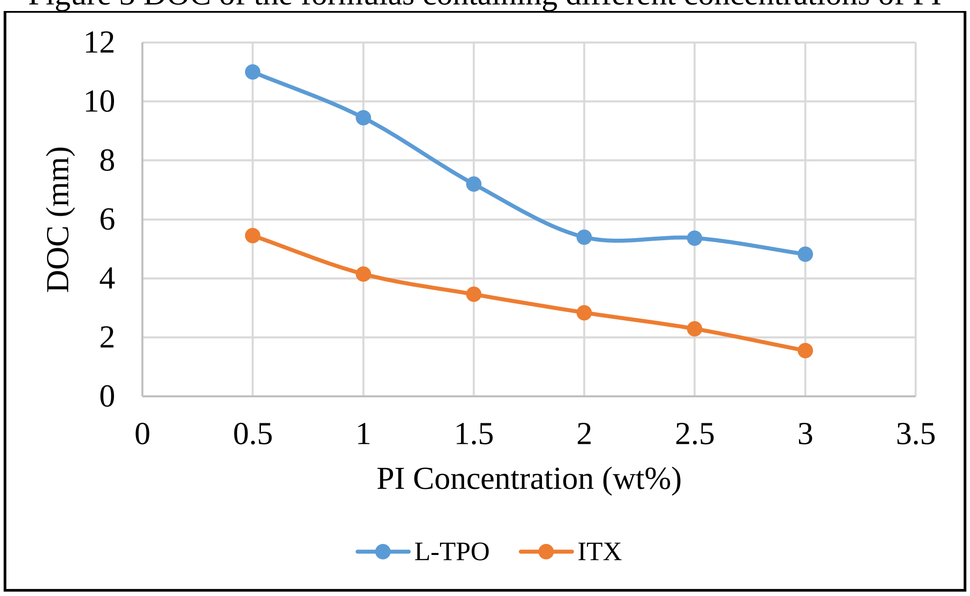
In this study, different concentrations from 0.5% to 3% of Type I phosphine oxide based visible PI Omnirad TPO-L and monomeric Type II PI thioxanthone Genocure ITX (ITX) were studied using the same resin compositions. For ITX , the amine synergist used is DMAPMA and ITX/DMAPMA weight ratio is 1:2. The previous samples 1.3 and 1.4 with 1% PI, and new samples 2.1-2.10 with other concentrations were cured using LED 405nm for 5s.

Table 6 is the summary of the DOC and surface tackiness of the formulas containing different concentrations of PI L-TPO and PI ITX, amine DMAPMA respectively. Figure 3 is a graph showing the correlation of DOC and PI concentration. Results in Table 6 and Figure 3 showed that DOC decreases with increasing PI concentration for both PIs. The trend is opposite for surface tackiness tests. High PI concentration is beneficial to tacky free surface. Comparing formulations with the same loading of TPO-L and ITX, DOC is lower with ITX, but formulation with ITX results in better in terms of surface tacky free.

Table 6 Summary of the DOC of the formulas containing different concentrations of PIs

PI	Sample	PI Concentration (wt%)	DOC (mm)	Surface tackiness
Omnirad TPO-L	2.1	0.5	11.00	Yes
	2.2	1	9.45	Yes
	1.3	1.5	7.20	No
	2.3	2	5.40	No
	2.4	2.5	5.37	No
	2.5	3	4.82	No
ITX/ DMAPMA	2.6	0.5	5.45	Yes
	1.4	1	4.15	No
	2.7	1.5	3.46	No
	2.8	2	2.84	No
	2.9	2.5	2.29	No
	2.10	3	1.55	No

Figure 3 DOC of the formulas containing different concentrations of PI



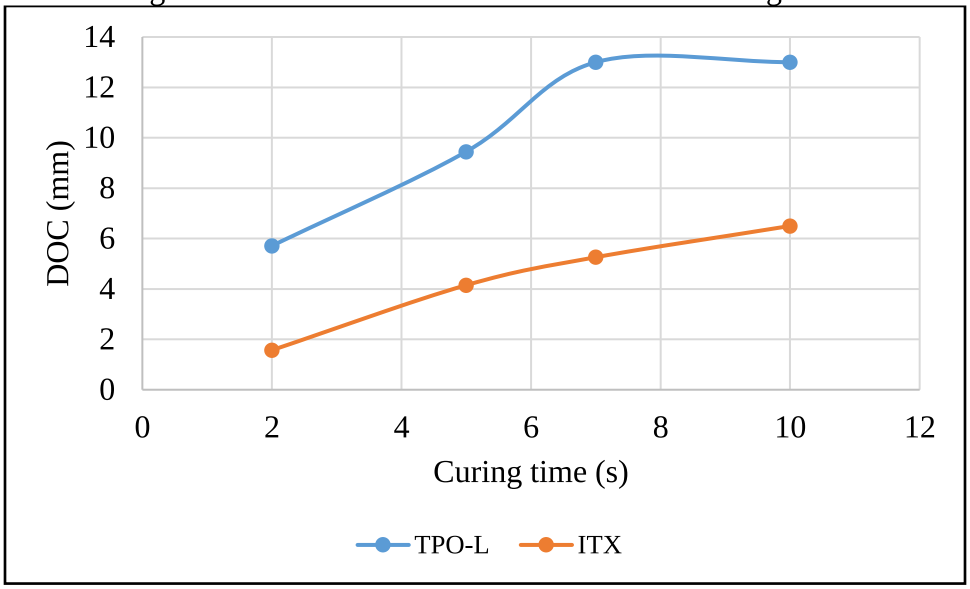
Curing time effect on DOC and Surface tackiness

In this study, two formulas Sample 1.3 with 1% L-TPO and Sample 1.4 with 1% ITX and 2% DMAPMA, were cured with LED 405nm for different time. Table 7 is the summary of the DOC and surface tackiness of the two formulas with different curing time. Figure 4 is a graph showing the correlation of DOC and curing time.

Table 7 Summary of the DOC and surface tackiness of the formulas with different curing time

Formula	Curing time (sec)	DOC (mm)	Surface tackiness
1.3	2	5.71	Yes
	5	9.45	Yes
	7	13.00	Yes
	10	13.00	Yes
1.4	2	1.57	Yes
	5	4.15	No
	7	5.26	No
	10	6.50	No

Figure 4 DOC of the formulas with different curing time



Results in Table 7 and Figure 4 showed that DOC increases with increasing curing time for both PIs. The DOC of Sample 1.3 showed DOC reached full depth of 13mm after 7 sec. The surface still showed tackiness after 10s curing due to the selected PI concentration. Increasing curing time in this case didn't improve surface curing.

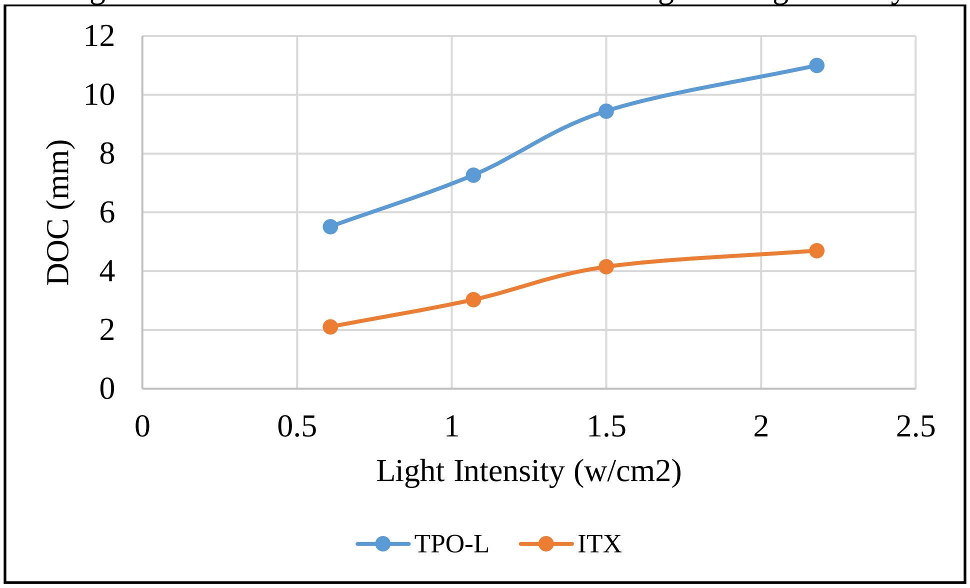
Curing light intensity effect on DOC and surface tackiness

The two formulas Sample 1.3 and 1.4 were cured with LED 405nm under different intensity for 5s. Table 8 is the summary of the DOC of the two formulas with different curing intensity. Figure 5 is a graph showing the correlation of DOC and curing light intensity. Results in Table 8 and Figure 5 showed that DOC increases with increasing curing light intensity for both PIs. The surface of Sample 1.3 still showed tackiness even with increased light intensity due to the selected PI concentration. For Sample 1.4, surface turned from tacky to non-tacky after curing intensity increases.

Table 8 Summary of the DOC and surface tackiness of the formulas with different curing intensity

Formula	Curing Intensity (W/cm^2)	DOC (mm)	Surface tackiness
1.3	0.61	5.52	Yes
	1.07	7.27	Yes
	1.5	9.45	Yes
	2.18	13.00	Yes
1.4	0.61	2.11	Yes
	1.07	3.03	Yes
	1.5	4.15	No
	2.18	4.70	No

Figure 5 DOC of the formulas with different light curing intensity



DOE study on formulations with ITX loading and DMAPMA/ITX ratio

In this study, the DOC and surface tackiness performance are optimized by design of experiment using rotatable central composite design (CCD), which is one of the designs in response surface methodology design. There are two factors used in RSM study.[9,10] Factor 1 is monomeric PI ITX loading ranging from 0.17% to 2.13% and factor 2 is the ratio of amine synergist (DMAPMA) to PI (ITX) loading ranging from 0 to 4.0. The RSM design comprises 4 factor points, 4 axial points and 3 replicates of central points with total of 11 runs. Adhesives are cured with 405nm LED light for 5 seconds. Response DOC is measured as above-mentioned technique. Response surface tackiness was quantified by the relative amount of SiC powder stayed on the cured adhesive surface after brushing. If no SiC powder sticky to the surface, it is rated as “0”, and if all powders stayed on the surface, it is rated as “10”. Any values in between 0-10 were estimated based on the amount of SiC powder on the surface. The RSM design points and response data are summarized in Table 9.

Table 9 Summary of the DOC and surface tackiness of the formulas containing different ITX loading and DMAPMA/ITX ratio

Std	ID	Run	Factor 1	Factor 2	Response 1	Response 2
			A:ITX loading	B:DMAPMA/ITX ratio	DOC (mm)	Surface tackiness
1	1	3	0.30	0.27	4.90	10
2	2	5	2.00	0.27	1.90	8
3	3	4	0.30	4.00	7.80	10
4	4	1	2.00	4.00	2.67	0
5	5	6	0.17	2.14	7.50	4
6	6	2	2.13	2.14	4.30	0
7	7	7	1.15	0.00	1.50	2
8	8	10	1.15	4.28	4.25	1
9	9	8	1.15	2.14	5.00	2
11	9	9	1.15	2.14	4.20	2
10	9	11	1.15	2.14	4.80	2

The results were analyzed by using Design Expert Version 11 software. Statistical analysis (regression and ANOVA analysis) of each response were carried out to determine the goodness of fit of each model and to estimate the coefficients of the polynomial equation. For response DOC, a reduced quadratic model was obtained with R^2_{adj} and R^2_{pred} of 0.905 and 0.789, respectively. For response surface tackiness, transformation with inverse square root was applied to have a linear model with R^2_{adj} and R^2_{pred} of 0.863 and 0.785, respectively. The final model equations are listed in Equation 1 for DOC and Equation 2 for surface tackiness. Their corresponding surface contour plots are shown in Figure 6.

Equation 1:

$$DOC = 5.917 - 5.166 * \text{ITX loading} + 2.173 * \text{amine/ITX ratio} + 1.337 * (\text{ITX loading})^2 - 0.380 * (\text{DMAPMA/ITX ratio})^2$$

Equation 2:

$$1/\ \text{Sqrt}(\text{tackiness}-0.5) = 0.066 + 0.536 * \text{ITX loading} + 0.038 * \text{DMAPMA/ITX ratio}$$

By applying multiple response optimization for maximum DOC and minimium surface tackiness, a high desirability of 0.7 is obtained to have predicted DOC of 5.6 mm and surface tackiness of 3.4. The optimized formulation is comprised of 0.84% of ITX and DMAPMA/ITX loading ratio of 3.14. The optimization desiability plot is shown in Figure 7.

Figure 6 Surface contour plots of response DOC and surface tackiness

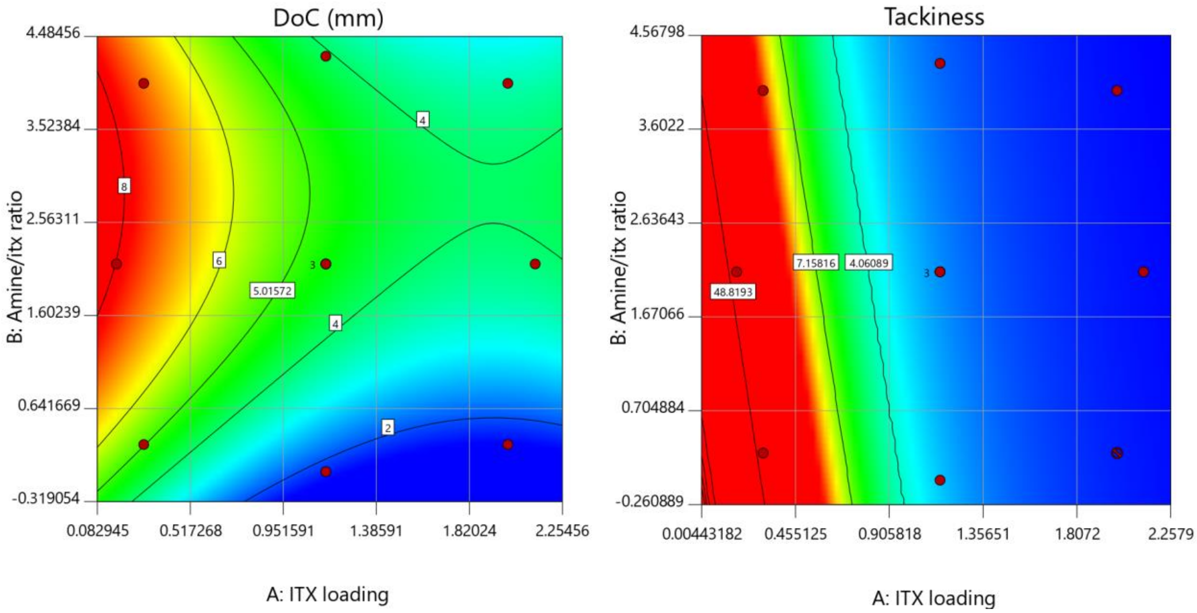
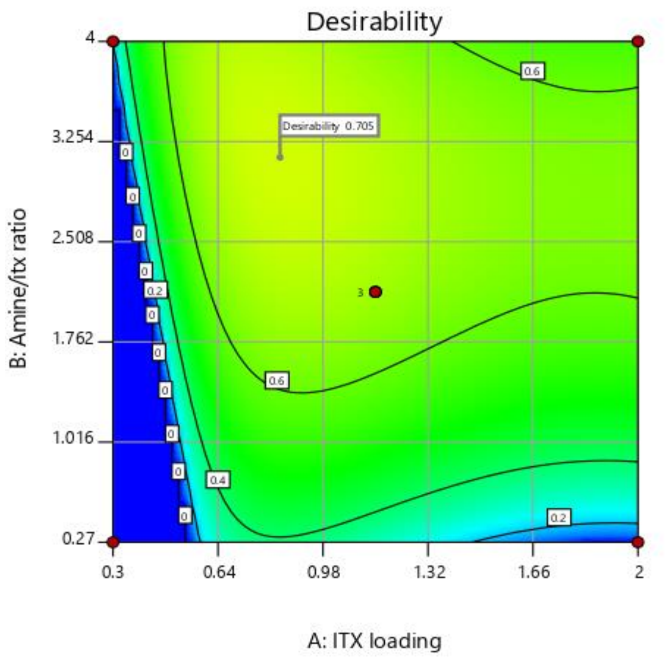


Figure 7 Optimization desiability plot for DOC and surface tackiness



Conclusions

This work examined the effect of visible photoinitiator type and concentration, as well as LED 405nm intensity and curing time on the depth of cure and surface tackiness of an acrylate resin system under LED 405nm light curing. UV/Visible absorption spectra of the visible photoinitiators were used to obtain the PI absorbance at 405nm. The 405nm absorbance of the six PIs tested at 0.01%

concentration has the order of: Omnipol TX>Genocure ITX>Omnirad 819>Omnirad TPO >Omnirad TPO-L>Genopol TX-2. The PI absorbance correlates to its photo curing reactivity. The study proved as literature reported that DOC decreases with increasing reactivity at 405nm, however, less surface tackiness was observed with increasing PI reactivity. With increasing PI concentration, the curing speed increased, which results in less oxygen inhibition and less surface tackiness. The DOC decreased with increasing PI concentration due to the light blocking from the polymer gel formed on the resin surface. DOC increases with increasing curing intensity and time as expected. Surface curing will be improved with curing time although the tests in the study didn't show any differences.

It is important to understand how these parameters work together in order to optimize the surface curing and depth of curing of the selected resin systems, and DOE is a good tool for this optimization process. DOE using RSM was able to optimize Type II PI ITX concentration and amine synergist DMAPMA/ITX ratio for the most desired surface curing and DOC. A high desirability of 0.7 is obtained to have predicted DOC of 5.6 mm and surface tackiness of 3.4 with optimized formulation comprising 0.84% of ITX and DMAPMA/ITX of 3.14.

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