

Use of Modeling to Optimize UV Solutions and Understanding

By Glen Thommes and Jeff Thommes

Suppose you could understand oxygen effects, through cure and some physical properties for your UV formulation or application through modeling, before going to the lab or experiencing production down time. Most would agree accelerating customer response time and product development would be a win for RadTech members and UV-product users. At the same time, however, the complexities of UV curing make practical modeling an extreme challenge, not to mention that fun in the lab and manufacturing is the best way to get “real results.” Besides, pulling the proverbial rabbit out of the hat provides great job security—right? Wrong. Market demands drive solutions with or without us. Consider how computer modeling transformed pharmaceutical product development, financial institutions and consumer purchases. But, can it work for something as complex as UV curing?

UV Modeling Challenges

Modeling UV curing is a daunting task; however, significant in-roads have been made and successful modeling of UV processes (formulation and systems) is on the verge of assuming center stage as a high-value driver for UV-market growth. Most agree that modeling is “interesting,” but is it a practical growth-driving addition for your business? Most in the industry are familiar with the effects that oxygen can have on a UV coating and

know we *must learn* to deal with it. Hopefully, this article will convince you that a new tool is available to improve productivity and support your UV-curing business.

Investigating Oxygen Examples

Decker and Moussa in a 1990 study¹ provided a wealth of data that can serve as a standard to compare with model-generated results, particularly in the area of dealing with the effects of oxygen inhibition. In this study, formulation films consisting of 5% photoinitiator and equal weights of an aliphatic polyurethane diacrylate oligomer and di-functional monomer 1,6-hexanediol diacrylate were mixed and cast as 20 micron thick films (Table 1). The films were exposed with an irradiance of 200 mW/cm² from a continuous wave Krypton ion laser at 337.4 nm for one second. The exposure was static and open to atmospheric air. The course of the photoreactions ensuing was followed with RTIR. Table 2 displays some key data taken from Decker and Moussa’s paper (D-M) and compares it to that generated by PrecisionCure’s modeling software.²

From Table 2, the following conclusions can be made:

- Rates of polymerization are closely approximated by the model.
- Conversion of acrylate groups at one second is also closely duplicated.
- The difference in rates observed and the extent of conversion at one second are impacted significantly

by oxygen inhibition (tacky surface thickness.)

The rate of polymerization is also affected by the fraction of the actinic radiation effectively absorbed and the quantum yield of active radical production for the system. The next evaluation compares the modeling software on all of these factors of consideration (and more) to actual kinetic measurements from the D-M paper and is displayed in Figure 1.

The fit of the model to the actual experimental data is very good and substantiates that the model produces directionally accurate results. Accepting this fact, how does one use the model to increase productivity?

Defining Solutions and 'Acceptable' Results

The results reviewed in Table 2 and Figure 1 demonstrate significant problems with oxygen inhibition for all formulations except Photoinitiator A sensitized formulation and possibly Photoinitiator B. In Photoinitiator B sensitized case, oxygen inhibition is recognizable, but may in a practical sense may be acceptable because it is so slight. It is possible that monomer diffusion to the polymerized interior could well "dry" the surface to an

TABLE 1

Photoinitiator formulations

Photoinitiator	
A	2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butanone-1
B	2-methyl-1[4-(methylthio) phenyl]-2-morpholinopropan-1-one
C	2,2-dimethoxy-1,2-diphenylethan-1-one
D	1-hydroxycyclohexyl phenyl ketone
E	2-hydroxy-2-methyl-1-phenyl-propane-1-one

"acceptable" level. This would need to be verified by physical testing in the laboratory. Faced with surface oxygen inhibition problems, the common reaction of one skilled in the art would be to increase the rate of radical production until it can effectively compete with the influx of oxygen. Or alternatively, block out oxygen by laminating an impenetrable (at least on the time scale of exposure) film to the surface or blanket the coating with an inert gas such as nitrogen or carbon dioxide. Both alternative approaches can be evaluated in the model. While both are clearly effective, they also require major changes in process that would add to production cost.

Consequently, the logical step is to increase the rate of active radical production. This involves one or more of the following alternatives:

- Finding an initiator with higher actinic absorption coefficient(s) or higher quantum yield for active radical production.
- Increasing the incident actinic radiation intensity (new lamp type or increasing irradiance).
- Increasing the concentration of the photoinitiator.

Optimizing Personal and Lab Time to Find 'Acceptable'

Can modeling efficiently help evaluate choices from the above

TABLE 2

Key data comparison

5% Photoinitiator	D-M Rate of Polymerization moles/liter-second	Modeling Rate of Polymerization moles/liter-second	D-M Degree of Conversion at one second	Modeling Degree of Conversion at one second	Modeling % of Surface Coating Lost to Oxygen	Modeling Microns Lost to Oxygen Tacky Surface Thickness
BP with Amine	4.7	4.5	46.5	43.5	38.2	7.64
A	21.0	25.2	87.4	83.7	0.0	0.00
B	15.7	18.3	83.9	82.7	0.4	0.08
C	14.8	15.25	79.9	78.5	5.7	1.14
D	11.5	12.0	68.0	72.3	13.3	2.66
E	9.5	10.2	64.0	67.2	19.6	3.92

options and can it quantitatively guide companies to an acceptable and improved solution? To examine this question, two of the formulations shown will be used to demonstrate how the modeling software described in this article can be used. Photoinitiator C and Photoinitiator B are the two examples in all virtual experiments. When either the photoinitiator or its “concentration” is changed, the choice and amount of monomer and oligomer are held constant. The benchmark for “acceptable levels” of cure is considered to be the original 5% Photoinitiator B formulation. It is assumed that what is desired is to understand a tolerance associated with varying exposure time, irradiance level and weights in the formulation to meet or exceed the “acceptable level” benchmark.

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FIGURE 1

D-M RTIR conversion vs. model generated

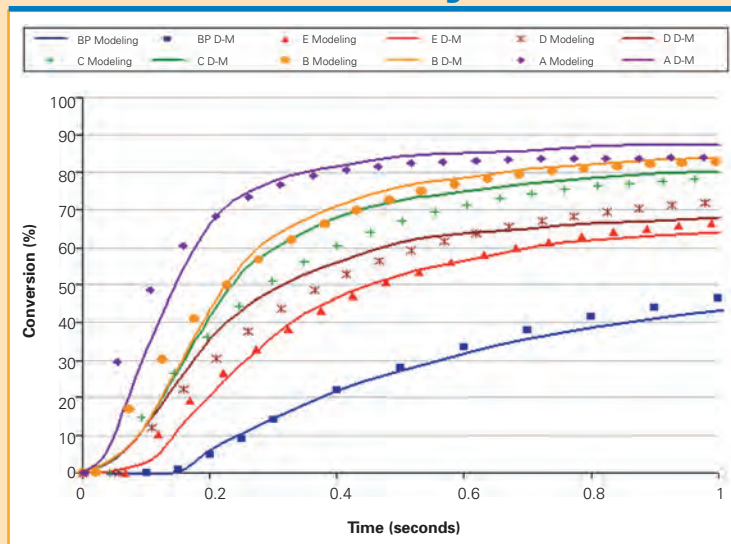


TABLE 3

Varied irradiance

5% Concentration Photoinitiator	Varied Irradiance Level mw/cm ²	Modeling Rate of Polymerization moles/liter-second	Modeling Degree of Conversion at 1 second	Modeling % of Surface Coating Lost to Oxygen
C	50	6.0	51.0	37.4
C	100	9.8	65.8	19.9
C	150	12.8	74.0	10.6
C	200	15.3	78.5	5.7
C	250	17.3	81.0	3.0
C	300	19.0	82.3	1.6
C	400	21.8	83.6	0.5
C	500	24.0	83.9	0.0
B	50	7.7	63.0	19.2
B	100	12.4	76.7	5.3
B	150	15.5	81.1	1.5
B	200	18.0	82.8	0.4
B	250	19.8	83.2	0.0
B	300	21.4	83.5	0.0
B	400	24.1	83.8	0.0
B	500	26.3	83.9	0.0

TABLE 4

Varied initiator concentration

Initiator at Irradiance Level 200 mw/cm ²	Varied Initiator Concentration	Modeling Rate of Polymerization moles/liter-second	Modeling Degree of Conversion at 1 second	Modeling % of Surface Coating Lost to Oxygen
C	1	5.4	45.7	41.6
C	3	11.3	69.5	15.1
C	4	13.5	75.0	9.2
C	5	15.3	78.5	5.7
C	6	16.7	80.8	3.5
C	7	17.9	82.4	2.2
C	12	21.7	85.3	0.0
C	15	23.5	86.0	0.0
B	1	8.8	61.6	23.8
B	3	15.4	79.7	3.0
B	4	17.0	82.1	1.1
B	5	18.0	82.8	0.4
B	6	18.5	83.1	0.0
B	7	18.8	83.5	0.0
B	12	18.9	83.9	0.0
B	15	18.3	83.8	0.0

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From Table 2, the minimum acceptable results from a one second exposure suggest achieving no more than 0.4% surface loss to oxygen and more than 82% conversion using the same irradiation source of the Krypton ion laser. Eight experiments were conducted for each of the two initiators, in one case, varying the initiator amounts and holding the irradiance level constant at 200 mw/cm². In a second case, the initiator amount was held constant (5%) while varying the irradiance level. In total, 32 experiments were conducted to profile the initiators and the conditions used to cure the formulations. Tables 3 and 4 demonstrate a summary of the experiments relating to the rate of polymerization, conversion and percent of coating lost to oxygen.

The shaded areas represent “acceptable levels” as defined previously

and show, with little surprise, that in both cases either increasing initiator amounts or irradiance levels improve radical production and ability to overcome oxygen. As might be expected from the original conversion curves in Figure 1, Photoinitiator B outperformed Photoinitiator C at a lower requirement for the amount of initiator. In fact, to match the performance of B, in this case, C levels were increased to nearly 10% of the formulation. In addition, as expected, a clear decrease in the surface effects of oxygen can be seen with an increase in irradiance. However, to improve C to achieve the original B levels the irradiance level would need to be doubled for the 5% initiator loading.

In addition to beginning to quantify parameters, a more subtle effect driven by the improved absorption fit with Photoinitiator B and the laser can also

be seen. Continuing to increase the initiator amount beyond 6% has little impact on improving “speed” as measured by the rate of polymerization for a given irradiance level. In fact, if the initiator concentration was increased too much, a reversal of the increasing average rate of polymerization can actually be seen. This is due in part to the fact that the absorption in the surface has increased enough to overcome oxygen, but the ability for the radiation to fully cure the base has decreased. Related to this effect, in the original parameters outlined, a minimum *average* conversion requirement for the formulation as well as a maximum level of oxygen effect acceptable at the surface was defined. Photoinitiator C at a loading above 6% begins to meet or exceed the minimum *average* RTIR type conversion. However, the conditions are not

sufficient to overcome oxygen at the surface. Utilizing RTIR data alone could have caused an interesting quality discussion between formulator, manufacturer and supplier. Finally, a diminishing return can be seen as it relates to increasing irradiance. This is evidenced by the fact that the rates of polymerization are asymptotically approaching a limiting value. Although not noted in this particular analysis, it can also be seen that increasing irradiance and/or initiator concentration will shorten average kinetic chain length and correspondingly impact physical properties.

Modeling for My Productivity

It would be fairly easy to continue the analysis to establish minimum “maximum” values of irradiance, time of irradiance (energy density), impact of thickness variances and other variables relating to irradiance levels and initiator types or concentrations.

Perhaps, alternate multi-chromatic radiation sources and blends of initiators in multiple ratios may be evaluated, which drastically decrease the ability to “intuitively” identify solutions and answers. All of this lends itself to modeling and can be done rapidly and at significantly reduced costs versus traditional lab methods. Consider that the 38 experiments discussed so far were generated in about an hour using modeling and not all of the directional outputs have been discussed. Besides, wouldn't it be better if physical properties were the outputs and more complex inputs were used? Stay tuned for a follow-up article scheduled for early next year.

Conclusion

Although there is still much to be developed with modeling, it seems apparent that uses of advanced modeling tools are ready to go. Still,

some may not be convinced of the value of modeling. Perhaps it is a threat or perhaps it's too much fun to develop “real data.” The good news is that labs are here to stay and can work exceptionally well in tandem with modeling. The only real threat is ignoring advancement and ending up as the MAC was to the PC in the 1990s—a better product that remained a small portion of the market for too long. ▀

References

1. *Makromol. Chem.* 191, 963-979 (1990), Kinetic investigation of photopolymerization induced by laser beams, Christian Decker, Khalil Moussa.
2. All modeling results produced by PrecisionCure LLC version 1.1 or higher, www.precisioncure.com.

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