Photoinitiator Polymer Systems: Multisurface Variance and Spectral Analysis

Leana Vitale, Leanavit@gmail.com

Department of Chemistry, Brookdale Community College

Mentor: Tanner Obrzut

Advisor: Nancy Cizin

May 2025

Abstract

Photoinitiator polymer manufacturers advise at least 60 seconds of curing time. However, spectral analysis may identify optimal curing increments with maximum bond interaction, potentially allowing for a lower curing time while maintaining high force resistance. The experiment presented here tested this using diphenyl (2,4,6-trimethylbenzoyl) phosphine oxide (TPO), hydroxycyclohexyl phenyl ketone (HCPK), benzophenone (Ph_2CO), and a non-photoinitiator control group. Spectral data, minimal curing time, and force withstood were reviewed for each sample on aluminum, birchwood, and borosilicate glass. The experiment found that all photoinitiator polymers showed the theorized best adhesion on borosilicate glass, with weak results on birchwood, and success with TPO on aluminum.

The Variance in Photoinitiator Polymer Systems

Polymers containing photoinitiators are used within a variety of industries, including dental, cosmetic, and creative for restorations, nail upkeep, and artwork. Bonding strength and curing times differ due to the variance of photoinitiators used within polymers. As, type 1 photoinitiators undergo unimolecular bond cleavage upon UV exposure to generate reactive species, beginning polymerization (Jędrzejewska & Pyszka 2024). While type 2 photoinitiators require a co-initiator such as an amine or alcohol functional group to undergo bimolecular bond cleavage to begin polymerization, often forming graft polymers. The applications of photoinitiator polymers can be expanded to industries such as construction and engineering, where they may serve as cost-efficient temporary aids to repair damaged hardware. The most optimal curing times on a variety of surfaces found through spectral graphs will show potential to cure varying photoinitiator groups at lower times, showcasing greater strength and binding ability compared to the ideal curing time of 60 seconds.

Materials and Methods

The photoinitiator polymer samples all came in the form of gel nail polishes containing white pigments and the monomer 2-Hydroxyethyl methacrylate (HEMA). Each polymer sample used different photoinitiators and was produced by different manufacturers. Including, ModelOnes®, believed to contain TPO (type 1), Orly®, containing HCPK (type 1), and Rosalind, containing Ph_2CO (type 2). The control group was a China Glaze® polish not containing monomers and photoinitiators. Sample surfaces included aluminum, borosilicate glass, and birchwood in the form of sheet metal, lab slides, and popsicle sticks.

Light absorption for each photoinitiator- containing polymer on the respective sample surfaces was tested in a Thermo Scientific Unity Lab Services Spectrophotometer, Nicolet iS5 with an iD5 tip. Before testing, the diamond tip and sample dish were cleaned with methanol and

kimtech wipes, while sample surfaces were cleaned with acetone. Light absorption was measured between 12 5-second increments of curing.

The SUNUV® Lamp, operating at 398 nanometers of UV and 405 nanometers of LED light, with the detachable mirror in use, was used to cure each sample.

Spectral data were reviewed to conclude the two most and least optimal curing times. Most optimal curing times were hypothesized where the most overlap in bond interaction was seen at a certain curing time increment, while the least optimal curing times were hypothesized where less bond interaction and stacking were seen within the graphs.

Figure 1

Hypothesized most optimal curing time

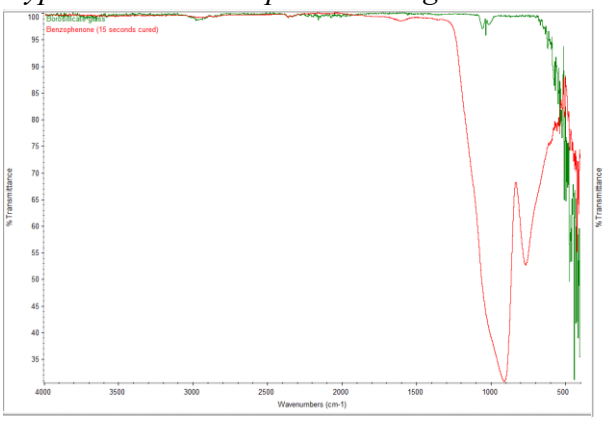
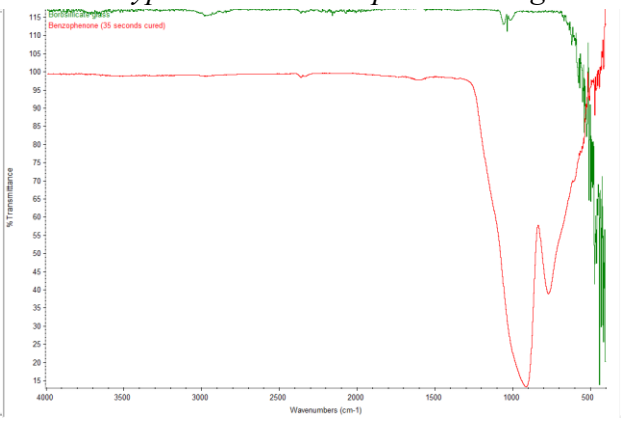


Figure 2

Hypothesized least optimal curing time



Holes were drilled into aluminum sheet metal and cut into birchwood popsicle sticks to allow access to the stainless-steel hook from the ANGEL POS® digital hanging scale for force testing. Sample surfaces were then bonded together with each different photoinitiator sample at the hypothesized most and least optimal curing times found, as well as the ideal curing time of 60 seconds. Once curing time concluded, force testing began. The holes in the aluminum and birchwood surfaces were accessed with the scale's hook. Borosilicate glass surfaces were held down to the scale's hook via a clamping force. A pulling motion of the scale's rubber handle was then employed, while a laboratory assistant held the end of the sample surface. All resultant

forces were recorded. Standard deviation and averages were calculated. Meanwhile, drying time was measured for the control group on each surface and underwent force.

Results

Ph_2CO showed a high of 2.5 lbs. of force withstood when bonded aluminum samples were pulled apart, showing an average of 0.68 lbs. when cured at the ideal of 60 seconds. Ph_2CO showed a high of 1.85 lbs. withstood when cured in the same duration of 60 seconds, with an average of 1.7 lbs.

Similarly, HCPK showed a high of 1.95 lbs. and an average of 0.95 lbs. with aluminum when cured for the hypothesized most optimal curing time of 20 seconds. With Birchwood, HCPK showed a high of 1.9 lbs. and an average of 1.15 lbs. when cured at the ideal time.

The TPO group on aluminum showed a high of 7.8 lbs. withstood when cured at 50 seconds, with an average of 4.47 lbs. However, on birchwood, the TPO group only withstood 0.95 lbs. when cured at the hypothesized most optimal curing time of 25 seconds, with an average of 0.92 lbs.

When force testing for borosilicate glass surfaces occurred, attempting to clamp sample surfaces to the scale caused some of the samples to shatter when the pulling motion occurred. All force results were indeterminate. A glass cutter was later purchased to attempt to cut holes into the glass surface, but all glass samples shattered during the cutting process due to the small surface area of the lab slides. However, after approximately one month had passed, the glass samples bonded together using the Ph_2CO group were able to be pulled apart with human force.

Discussion

The strength of the photoinitiator samples used within the experiment proves that photoinitiator polymers can be introduced to the industries of construction and engineering to temporarily repair damaged hardware. The polymer sample containing TPO showed the best bonding ability to aluminum when cured at 50 seconds, withstanding forces between 4.9-10.7 lbs. It is speculated that TPO showed the greatest results on aluminum as it is a type 1 photoinitiator known for its ability to effectively cure higher viscosity solutions. TPO likely performed best on aluminum because HCPK was in a low viscosity solution, and Ph_2CO, a type 2 photoinitiator, likely experienced improper curing and graft polymer formation in the monomer's higher viscosity. Safety data sheets indicated 28-day aerobic biodegradability for the photoinitiators. Interestingly, all borosilicate glass samples cured in 15-20 seconds remained strongly adhered, resisting manual separation till approximately 30 days. On aluminum and birchwood, groups often showed the greatest force standing ability when cured between 40-60 seconds, rejecting the hypothesis that spectral data always accurately shows the best curing time based on molecular interaction. Furthermore, bond adhesion was incredibly weak with birchwood, for the polymer seeps into the porous surface, not allowing proper binding.

While some results were favorable, errors occurred in the lab could have contributed to a skew in results. It is possible that the SUNUV® lamp did not take accurate time measurements, possibly leading for polymers to be cured longer than recorded. Furthermore, florescent lights in the laboratory were on during experimentation. As 20% of florescent lighting is speculated to contain UV wavelengths, curing could have begun prematurely. Last, proper force testing for bonded borosilicate glass was not possible at the time of the experiment. Surface area of borosilicate glass used in the study was too minimal, leading to shattering when holes were attempted to be cut. With these errors, it is suggested that future study be employed.

On the other hand, a study completed in 2022 by manufacturing engineer Joel Zarate concluded that polymers containing the photoinitiator Bis (2,6-Difluoro-3-(1-Hydropyrrol-1-Yl) Phenyl) Titanocene showed significant use in the engineering industry for its benefits in 3-dimensional printing. Models printed with the photoinitiator using the monomer ethylene glycol successfully cured using visible light and did not show signs of staircasing within models (Zarate et al.,2022). Meanwhile, operations researcher Dan Zhang found that triglycerides within tung oil act as natural photoinitiators, benefiting the rapid polymerization of wood wax oil for the woodworking industry (Zhang et al, 2023). Based on the findings in the studies of Zhang and Zarate, as well as the experiment completed, it is recommended that further study be done on photoinitiator polymers to continue to widen their use.

Conclusion

In this fundamental study, 3 photoinitiator polymers were tested to see if a curing time below 60 seconds was more optimal, and how much force each surface sample can withstand when bonded together using each photoinitiated polymer. It is concluded that all groups showed the best bonding ability to borosilicate glass due to its high surface energy and transparency, despite force results being indeterminate. The high surface energy of glass significantly influences post-polymerization adhesion, as silanol groups interact strongly with polar regions of the polymer, leading to greater adhesion. While transparency allowed for UV rays to adequately penetrate, allowing for proper curing, which likely did not happen with aluminum. With this, glass sample surfaces showed effective adhesion till an estimated 30 days had passed.

The group containing diphenyl (2,4,6-trimethybenzoyl) phosphine oxide showed the greatest force withstood on aluminum, while other groups only withstood forces of 1- 2 lbs. This is likely due to the diphenyl (2,4,6-trimethylbenzoyl) phosphine oxide photoinitiator being able

to promote full polymerization in higher viscosity substances, while other groups, such as Benzophenone, are prone to heat trapping, not fully completing polymerization.

While spectral data did not always convey optimal curing time, successes were found within each group, as each was able to show great strength when bonded to borosilicate glass. Results convey that photoinitiator polymers can be temporarily used as aids to repair hardware in the industries of engineering and construction. However, it is recommended that future study be employed to continue to widen the use of photoinitiator polymers.

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