

Experimental Comparison of Various Anti-Oxygen Inhibition Strategies in LED Curing

Branislav Husár/Institute of Applied Synthetic Chemistry, Vienna University of Technology/Vienna, Austria

Samuel Clark Ligon[§]/Institute of Applied Synthetic Chemistry, Vienna University of Technology/Vienna, Austria

Harald Wutzel/Institute of Applied Synthetic Chemistry, Vienna University of Technology/Vienna, Austria

Helmuth Hoffmann/Institute of Applied Synthetic Chemistry, Vienna University of Technology/Vienna, Austria

Robert Liska[§]/Institute of Applied Synthetic Chemistry, Vienna University of Technology/Vienna, Austria

[§] Christian Doppler Laboratory (Photopolymers in digital and restorative dentistry)

Abstract

Photocuring of coatings with LEDs in air suffers from the detrimental effect of molecular oxygen causing low double bond conversion and poor properties of a cured coating. The objective of this study is to assess the performance of various anti-oxygen inhibition strategies by comparing double bond conversions at low light intensities.

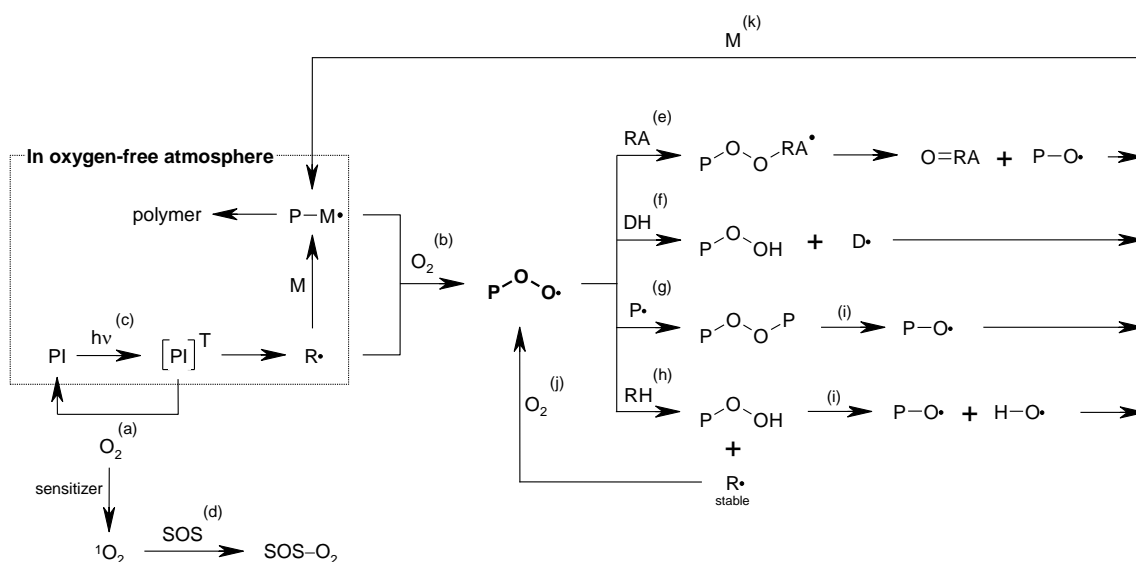
1. Introduction

UV curable coatings based on the radical polymerization of acrylates are an increasingly popular alternative to traditional solvent-borne coatings. However, the problem of the inhibition of radical polymerization by ground state molecular oxygen has not been solved yet. Incomplete curing leads generally to diminished mechanical performance and tacky surfaces [1]. In the coatings industry, this problem has been traditionally mitigated by using a combination of two photoinitiators, whose absorption characteristics match the emission bands of the mercury lamp. This method is inapplicable when light emission diodes (LEDs) are employed.

To overcome the associated problems of oxygen inhibition, manufacturers are often reliant on rather costly nitrogen inerting. Utilization of wax additives, liquid barriers, or lamination are inappropriate for the SME end users. Another way to reduce oxygen inhibition is to increase curing light intensity but this option is limited to certain threshold, above which termination overtakes propagation.

Additive based anti-oxygen inhibition strategies can be classified according to the role or roles they play on the reactions of photoinitiation, radical polymerization, and associated side reactions with oxygen (Scheme 1). Formation of unreactive peroxy radical (POO•) can be minimized by reducing the concentration of oxygen during or prior to initiation. This can be achieved e.g. by addition of sensitizers in combination with singlet oxygen scavengers or inert gas producing compounds [2, 3]. If oxygen is not completely removed prior to initiation, all is not lost. Hydrogen donors can react with POO• to form a reactive radical (D•) capable of propagating polymerization or alternately scavenging an additional

molecule of oxygen. Typical hydrogen donors are amines [4], thiols [5], and ethers [6] but also less common silanes [7], stannanes [8], hydrogen phosphites [9], or aldehydes [10]. Unreactive peroxy radicals ($\text{POO}\cdot$) can also be transformed by reducing agents to a new reactive radical ($\text{PO}\cdot$) that may propagate polymerization. Typical representatives of this group of reagents are phosphines [11], phosphites [12], boranes (which are often complexed with amines to improve stability) [13]. Finally, strategies to regenerate radicals by decomposing peroxide species with photosensitizers are considered [14]. Strategies based on modification to the monomer formulation may not be accurately depicted by Scheme 1 explaining the role of additives. Such strategies include acrylates bearing aforementioned reactive functional groups [6], multifunctional acrylates [15], acrylated dendrimers [16], *N*-vinyl amides [17], donor/acceptor type monomers [18], and hybrid radical/cationic systems [19].



Scheme 1. Mechanistic explanation of oxygen inhibition and strategies to mitigate it: (a) quenching of excited state of photoinitiator, (b) formation of unreactive peroxy radicals from initiating or propagating radical, (c) initiation stage strategies (i.e., inerting, lamination, light source, molecular inerting, and photoinitiators), (d) singlet oxygen scavengers, (e) reducing agents, (f) hydrogen donors, (g) termination by radical–radical recombination, (h) hydrogen abstraction, (i) peroxide decomposition, (j) scavenging of a molecule of oxygen, and (k) reinitiation of polymerization.

In this study, we attempted to assess the effectiveness of various anti-oxygen inhibition additives by determination of the DBC of the cured additive containing formulation and comparing to the DBC of the cured base (additive-free) formulation. FTIR is a precise and quantitative method for assessing cure performance, but it is limited at high conversions where DBC may not correlate well with the mechanical properties of the cured coating [20].

2. Experimental

The base formulation consisted of a 1:1 w/w mixture of polyether urethane diacrylated (Bomar BR-344) and DPGDA with 2 wt% of Speedcure BDMB as a photoinitiator. Various additives were then added to this base formulation in amounts expressed in molar equivalents to BDMB. Freshly prepared films (6 μm) on polyethylene foil were placed into the FTIR spectrometer and irradiated for 10 s with LED lamps. Sample films without ITX were irradiated the 365 nm LED lamp (120 mW/cm^2 at the

surface of the film). For samples prepared with ITX, the film was irradiated simultaneously with 365 and 400 nm LED lamps ($2 \times 60 \text{ mW/cm}^2$ at the surface of the film). All measurements were performed at least 5 times to ensure the reproducibility of the results. Finally, double bond conversion (DBC) was determined from the decrease of the 1620 and 1637 cm^{-1} bands using the carbonyl band at 1726 cm^{-1} as a reference.

3. Results and Discussion

The results are summarized in Figure 1 and 2. Figure 1 shows the results acquired after curing at 365 nm in air. The full line displays the DBC (27%) achieved from the curing of the base formulation under air without any additive. The dashed line shows the DBC (79%) obtained from the same base formulation cured under laminated conditions. Data presented in Figure 2 were obtained after dual-wavelength curing at 365/400 nm in air. The addition of ITX (0.14 wt%) increases DBC of the base formulation from 27% (365 nm) to 42% (365/400 nm) at the same total light intensity and dose. The full line displays the DBC (42%) achieved after curing in air, while the dashed line shows the DBC (84%) under laminated conditions.

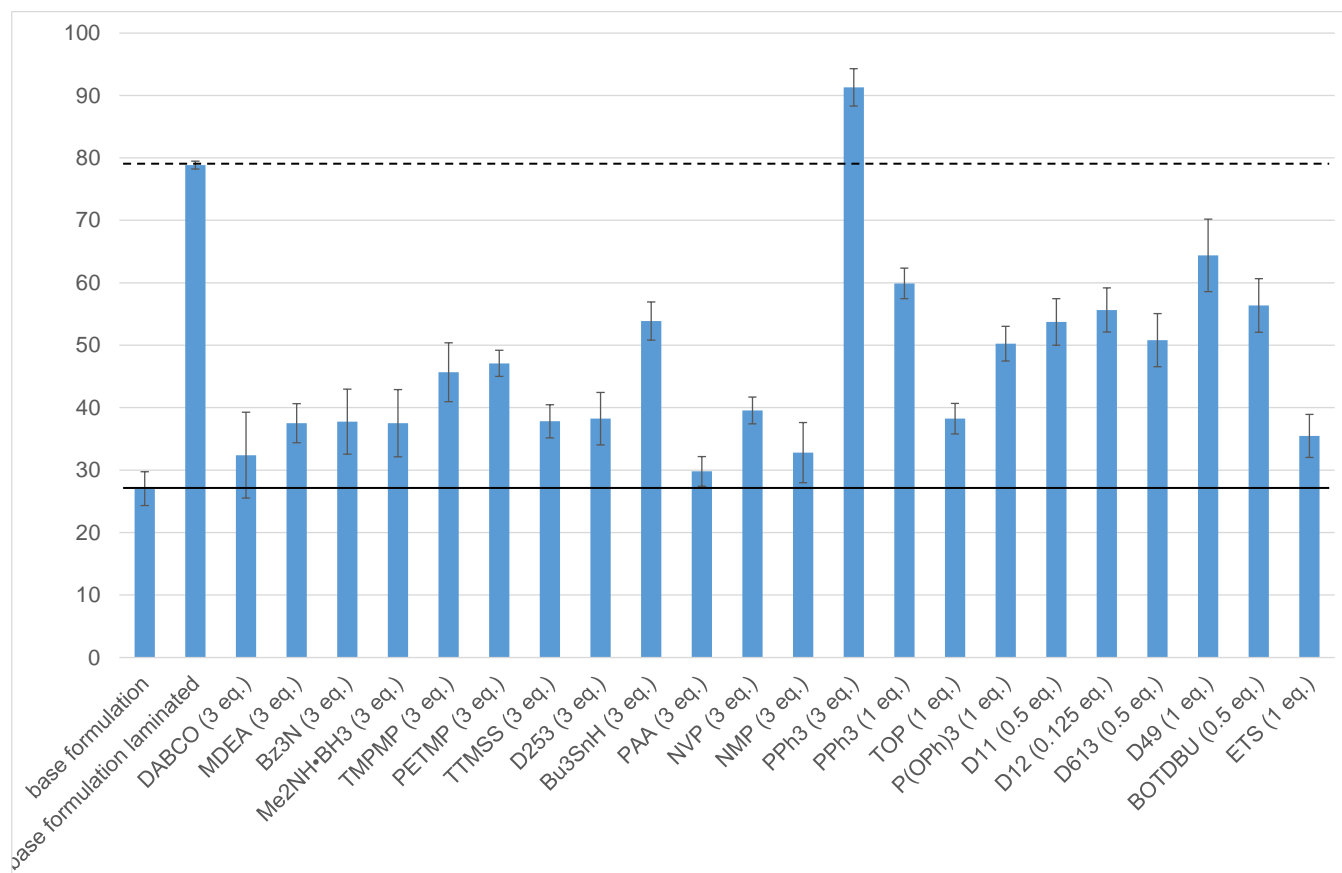


Figure 1. Double bond conversions of formulations containing various additives cured at 365 nm in air.

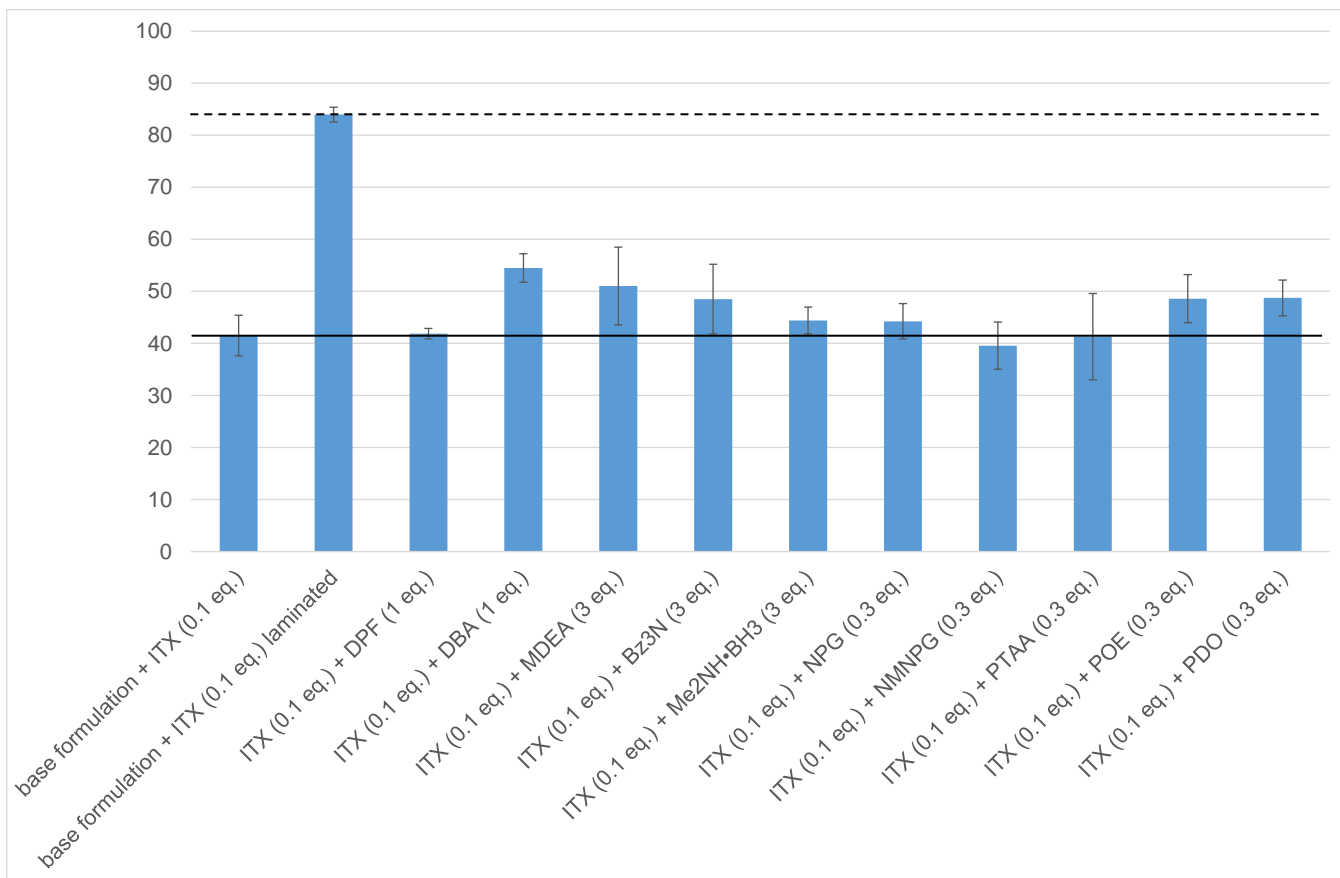
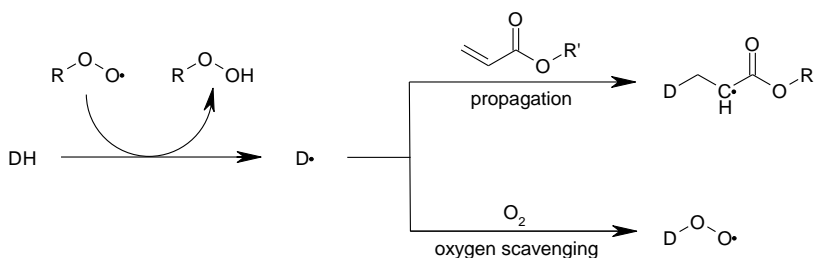


Figure 2. Double bond conversions of formulations containing ITX as sensitizer and various additives cured simultaneously at 365/400 nm in air.

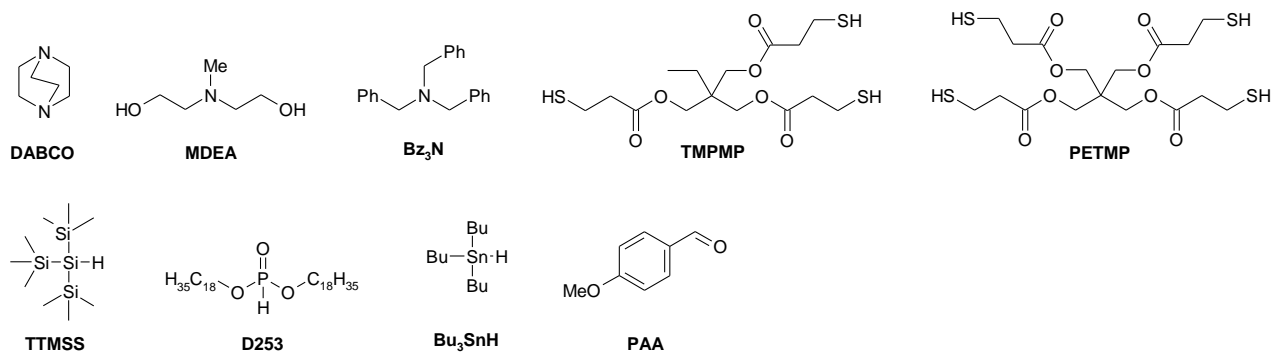
3.1 Hydrogen Donors

A general scheme for the mechanism of hydrogen donation is shown in Scheme 2. The hydrogen donor donates a hydrogen atom, which caps the already formed peroxy radical. The formed donor radical ($D\cdot$) reinitiates polymerization or scavenges a molecule of O_2 .



Scheme 2. Radical reinitiation via hydrogen donation.

In this study, a series of hydrogen donors (amines, thiols, silane, hydrogen phosphite, stannane, aldehyde) has been tested (Scheme 3).



Scheme 3. Tested hydrogen donors.

N-methyl diethanolamine (MDEA) and tribenzyl amine (Bz₃N) were found more effective than 1,4-diazabicyclo[2.2.2]octane (DABCO). Addition of MDEA and Bz₃N to the formulation increased the DBC from 27% to 38%, while with DABCO only 32% DBC was reached. MDEA is thus preferred since Bz₃N is a solid and has a much high molecular weight. In the presence of ITX, MDEA gives similar enhancement with DBC increasing from 42% to 51%. Bz₃N by comparison seems to be less effective in the presence of ITX. Odor, volatility, water solubility, and reactivity with atmospheric acids are issues with low molecular amines. Therefore, amine acrylate monomers are a good alternative.

Thiols are effective hydrogen donors and oxygen scavengers. In this study, a trithiol (TMPMP) and a tetrathiol (PETMP) were used. These multifunctional thiols copolymerize and therefore do not leach from the final coating. In comparison to amines tested at equal molar concentrations, TMPMP and PETMP provided superior results (46% and 47% DBC respectively). The main problems associated with thiols are their bad odor and their low storage stability. The problem of odor can be overcome by using polymeric thiols lacking cleavable groups. Storage stability can be improved with use of appropriate radical inhibitors and phosphonic acid coadditives [21].

Hydrogen phosphites HP(O)(OR)₂ have been scarcely reported as anti-oxygen inhibition additives [9]. In this study, dioleoyl hydrogen phosphite (D253) provided an enhancement in cure comparable to MDEA (38% DBC). Thus, no advantage over amines can be seen.

Silanes were reported to be effective hydrogen donors [8]. Tris(trimethylsilyl)silane (TTMSS) has Si–H bond energy (79.8 kcal·mol⁻¹) considerably lower than the C–H bond energy in MDEA (87.1 kcal·mol⁻¹). Despite that, TTMSS gives an improvement comparable to MDEA. TTMSS is air and water sensitive, heavier, and more expensive. Amines seem to be the better option.

Tributyl stannane (Bu₃SnH) contains a very weak Sn–H bond (73.8 kcal·mol⁻¹) and donates H-atom to peroxy radical about 10 times faster than TTMSS [8]. Although Bu₃SnH partially hydrolyzed in non-dried base formulation, the curing reached as much as 54% DBC. Despite a superior improvement, Bu₃SnH is not of industrial interest due to high toxicity and high moisture sensitivity.

Aldehydes have been described as effective coinitiators in Type II initiating systems [10]. In this study, aldehydes were tested as hydrogen donors in the presence of a Type I initiator. Addition of PAA did not provide a statistically significant improvement to the base formulation.

3.2 Reducing Agents

Reducing agents are capable of reducing peroxy radicals. In the process, new radicals are formed that may propagate reaction. Various phosphines, phosphites, sulphite, and borane were tested (Figure 3).

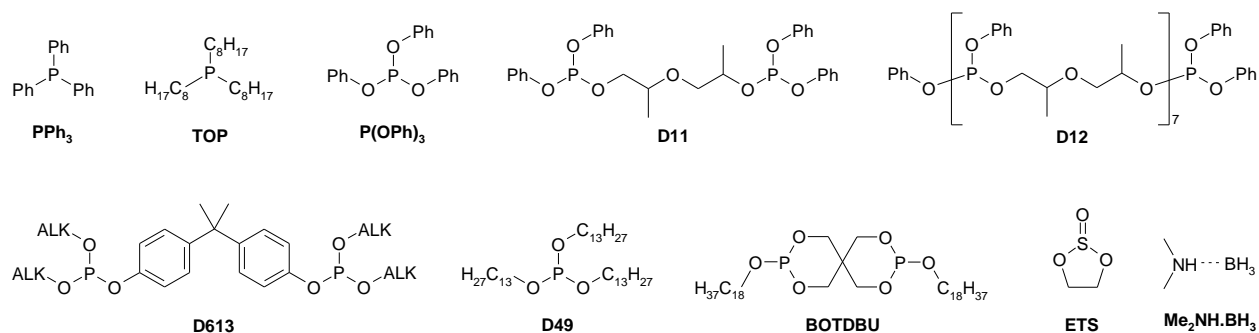
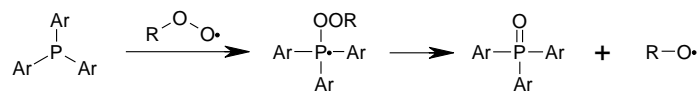


Figure 3. Tested reducing agents.

Phosphines and phosphites are very effective antioxidants. In photopolymerization, they may be oxidized by peroxy radicals. In the process, phosphine/phosphite oxides and alkoxy radicals are formed that reinitiate the polymerization (Scheme 4).



Scheme 4. Radical reinitiation via phosphine oxidation.

Triphenyl phosphine (PPh₃) is one of the most effective additives in this study. Under the testing conditions, 3 eq. gives a curing performance beyond that of the laminated sample (91% DBC) with no final surface tack. A freshly prepared formulation containing 1 eq. of PPh₃ gives 60% DBC, which decreased to 52% after 4 weeks of storage at room temperature in a sealed flask under air. Some turbidity and increased viscosity was observed. Moreover, when stored in an unsealed flask in air, approximately 10% of the initial acrylate groups in the formulation had vanished although the formulation did not gel. An aliphatic trioctyl phosphine (TOP) proved to be much less effective than PPh₃. DBC reached only 38%.

Phosphites proved to be the second most effective type of additive giving impressive results ranging from 50 to 64% DBC. The aromatic triphenyl phosphite (P(OPh)₃) was the least effective (50% DBC) that can be attributed to the reaction with alkoxy radicals to form unreactive phenoxy radicals. On the other hand, the aliphatic tris(tridecyl) phosphite (D49) gave the highest DBC in this study (64%). Phosphites are generally liquids and easy to dissolve in the formulation. Only BOTDBU is a solid and rapidly precipitates from the formulation. Price, viscosity, and color appear to be sufficiently low for wood coating applications. However, phosphites exhibit storage stability problems in some ways comparable to PPh₃. A slightly higher viscosity and turbidity was observed upon storage in a sealed flask under air for 4 weeks. In the case of the oligomeric D12, the DBC dropped from 56% to 44% after 4 weeks of storage. It is worth noting that phosphites also have a distinct phenolic odor independent of molecular weight, which could be detected even in the least volatile oligomeric D12.

Sulfites are known antioxidants but have not been reported to date as anti-oxygen inhibition additives for photopolymerization. As a representative of this class of molecules, we chose ethylene sulfite (ETS). Based on these results, the mediocre performance (36% DBC) and irritancy make them less appealing for industrial application.

Boranes in the presence of oxygen act as radical initiators. A useful strategy for stabilizing boranes during storage and yet to keep it available for intended oxygen inhibition is to complex it with an amine [13]. In the presence of a Type II photoinitiator, H-abstraction from the amine takes place. Released borane (BH₃) provides reactive radicals after the reaction with dissolved oxygen. We attempted to use the dimethylamine-borane complex (Me₂NH·BH₃) with a Type I photoinitiator (BDMB) only. The effect was comparable to that of amines (38% DBC). Surprisingly, in the presence of ITX (0.1 eq.) the increase in DBC was negligible. Under these conditions the effect of boranes is questionable and may not justify its use in light of issues such as cost, stability, and solubility.

3.3 N-Vinyl Amides

N-vinyl pyrrolidone (NVP) has often been added to UV curable resins to reduce viscosity and improve the curing in air. It has been suggested that (i) NVP acts as an oxygen scavenger similar to amines or (ii) NVP forms an exciplex with oxygen to produce reactive radicals or (iii) NVP forms a donor-acceptor complex with acrylate [17]. NVP gives 40% DBC while its non-vinyl analogue NMP gives just 33% DBC after curing in air. Although NVP seems to be an effective additive, similar results can be obtained with low molecular additives of similar molecular weight. Butyl acrylate gives 36% DBC and butyl acetate gives 34% DBC under the same curing conditions. These results can be explained by increased mobility of monomers. One must be also aware of increased hydrophilicity of the cured photopolymer, which is generally undesirable in wood coating applications.

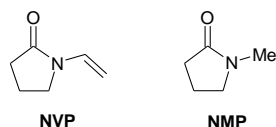


Figure 4. N-vinyl pyrrolidone (NVP) and N-methyl pyrrolidone (NMP).

3.4 Molecular Inerting

Some radical photoinitiators (Figure 5) undergo decomposition to provide initiating radicals and a molecule of CO₂. This gas has a potential to suppress oxygen inhibition by replacing oxygen in the formulation. These compounds are used in combination with a photosensitizer such as ITX and decompose according to the following scheme (Scheme 5).

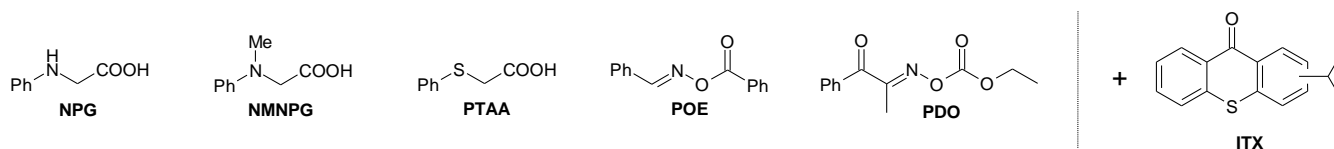
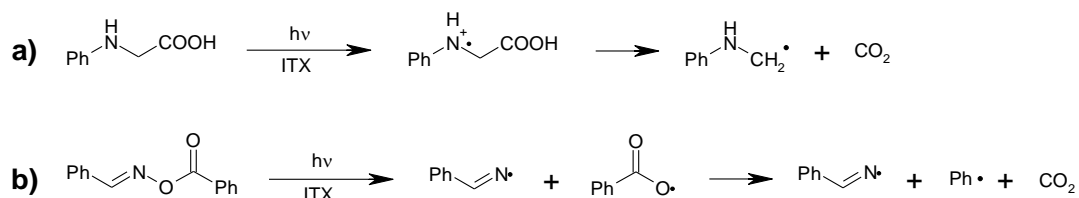


Figure 5. Tested CO₂ producers and sensitizer (ITX).



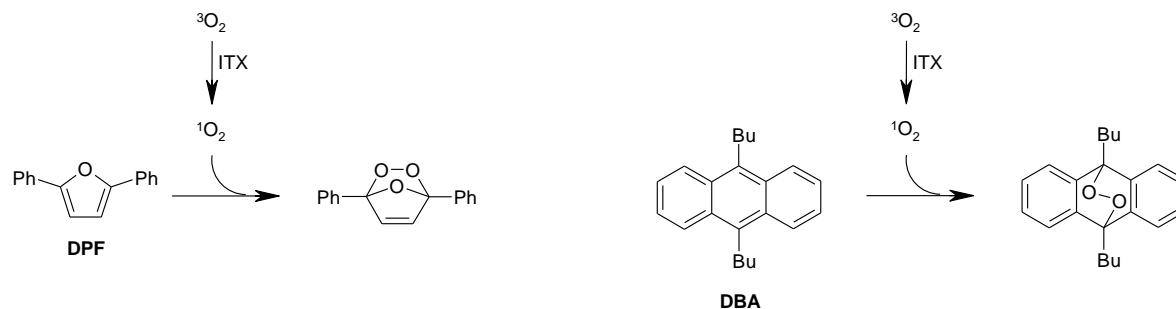
Scheme 5. Photo-induced gas generation from a) *N*-phenyl glycine (NPG) and b) *O*-benzoyloxime benzaldehyde (POE).

NPG, NMNPG and PTAA showed all negligible improvements in DBC after curing. ITX would be ideally used in equimolar ratio to these compounds, however it is not possible due to non-photobleachable nature of ITX.

Oxime esters (POE, PDO) seem to be a promising strategy at first, with improvement in DBC from 42 to 49% at low additive content (0.3 eq.). POE and PDO are also photoinitiators absorbing at 365 nm similarly to BDMB. However, addition of 0.3 eq. BDMB to base formulation with 0.1 eq. ITX improves curing to 55% DBC.

3.5 Singlet Oxygen Scavengers

Singlet oxygen ($^1\text{O}_2$) does not react with radicals during the polymerization process. $^1\text{O}_2$ can be generated from $^3\text{O}_2$ by a suitable photosensitizer, e.g. ITX. Due to the short life-time of $^1\text{O}_2$, it is essential to trap it before it can relax back to $^3\text{O}_2$. This is accomplished by using singlet oxygen scavengers, which undergo [4+2] cycloaddition reactions (Scheme 6).



Scheme 6. Singlet oxygen scavenging via [4+2] cycloaddition with diphenyl furan (DPF) and dibutyl anthracene (DBA).

In previous investigations, 2,5-diphenyl furan (DPF) gave very promising results in a formulation containing camphorquinone as the initiator reaching the same DBC in air as the formulation without DPF cured under nitrogen [2]. However, in this study the use of DPF without or with ITX did not increase double bond conversion. The usage of 9,10-dibutyl anthracene (DBA) in combination with ITX improved DBC from 42% to 55%. Important to clear coat applications, DBA photobleaches upon curing and the photoproduct is a stable molecule. DBA showed good storage stability in the formulation within 30 days.

Conclusions

To provide an alternative to nitrogen inerting, a variety of anti-oxygen inhibition additives were evaluated. Reducing agents are the most effective additives in improving final cure, however formulations are in almost all cases not storage stable. Hydrogen donors were found to improve cure up to a certain extent but due to different limitations only amines, borane-amine complexes and thiols seem applicable industrially. *N*-vinyl amides are suitable for applications where increased hydrophilicity and reduction in viscosity can be accepted. CO₂ producers provided only little improvement. The use of singlet oxygen scavengers seems to be a promising approach.

Acknowledgements

The authors wish to thank the European Commission for financial support of the FP7 SME project “Energy efficient UV LED curing without inerting” (Grant No. 262514). B.H. and R.L. gratefully acknowledge the support by the European Commission in the framework of Marie Curie Intra-European Fellowships through the project VINDOBONA (Grant No. 297895). Additional thanks for kind donation of chemical additives go to Lambson Ltd. (photoinitiators), Bomar Specialties (oligomer), Bruno Bock Chemische Fabrik (thiols), and Dover Chemical Corporation (phosphites).

References

- [1] S.C. Ligon, B. Husár, H. Wutzel, R. Holman, R. Liska, Strategies to Reduce Oxygen Inhibition in Photoinduced Polymerization, *Chemical Reviews*, 114 (2014) 557-589.
- [2] M. Höfer, N. Moszner, R. Liska, Oxygen scavengers and sensitizers for reduced oxygen inhibition in radical photopolymerization, *Journal of Polymer Science Part A: Polymer Chemistry*, 46 (2008) 6916-6927.
- [3] S. Jauk, R. Liska, Photoinitiators with Functional Groups 9: New Derivatives of Covalently Linked Benzophenone-amine Based Photoinitiators, *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry*, 45 (2008) 804-810.
- [4] G.L. Collins, J.R. Costanza, Reactions of UV curable resin formulations and neat multifunctional acrylates. II. Photoinitiated polymerization of neat 1,6-hexanediol diacrylate., *Journal of Coatings Technology*, 51 (1979) 57-63.
- [5] N.B. Cramer, C.N. Bowman, Kinetics of thiol-ene and thiol-acrylate photopolymerizations with real-time fourier transform infrared, *Journal of Polymer Science Part A: Polymer Chemistry*, 39 (2001) 3311-3319.
- [6] T.Y. Lee, C.A. Guymon, E.S. Jönsson, C.E. Hoyle, The effect of monomer structure on oxygen inhibition of (meth)acrylates photopolymerization, *Polymer*, 45 (2004) 6155-6162.
- [7] J. Lalevée, M.A. Tehfe, F. Morlet-Savary, B. Graff, X. Allonas, J.P. Fouassier, Radical photopolymerization reactions under air upon lamp and diode laser exposure: The input of the organosilane radical chemistry, *Progress in Organic Coatings*, 70 (2011) 83-90.
- [8] M. El-Roz, J. Lalevée, X. Allonas, J.P. Fouassier, Mechanistic Investigation of the Silane, Germane, and Stannane Behavior When Incorporated in Type I and Type II Photoinitiators of Polymerization in Aerated Media, *Macromolecules*, 42 (2009) 8725-8732.
- [9] B. Xiao, Y. Zhou, S. Li, M. Luo, X. Wang, P. Zhao, Studies on curing effect of phosphite monomer by EB radiation in the air, *Radiat. Phys. Chem.*, 57 (2000) 421-424.
- [10] J. Le Guern, H. Farge, X. Allonas, J. Lalevée, J.P. Fouassier, Method for free radical polymerisation and radiation polymerizable composition obtained by said method, in, A et A Mader; Centre National de la Recherche Scientifique; Université de Haute Alsace, 2009.
- [11] C. Belon, X. Allonas, C. Croutxé-Barghorn, J. Lalevée, Overcoming the oxygen inhibition in the photopolymerization of acrylates: A study of the beneficial effect of triphenylphosphine, *Journal of Polymer Science Part A: Polymer Chemistry*, 48 (2010) 2462-2469.
- [12] W. Schmitt, R. Purmann, P. Jochum, Photopolymerizable compositions based on acrylic or methacrylic acid esters containing organic phosphites, in, ESPE Fabrik Pharmazeutischer Praeparate GmbH, US, 1980.
- [13] A.V. Fedorov, A.A. Ermoshkin, A. Mejiritski, D.C. Neckers, New Method To Reduce Oxygen Surface Inhibition by Photorelease of Boranes from Borane/Amine Complexes, *Macromolecules*, 40 (2007) 3554-3560.

- [14] F. Morlet-Savary, F. Wieder, J.P. Fouassier, Sensitized dissociation of peroxides and peresters in the presence of thiopyrylium salts, *Journal of the Chemical Society, Faraday Transactions*, 93 (1997) 3931-3937.
- [15] L. Feng, B.I. Suh, Acrylic resins resisting oxygen inhibition during free-radical photocuring. I. Formulation attributes, *Journal of Applied Polymer Science*, 112 (2009) 1565-1571.
- [16] D. James, Unique Characteristics of a Dendritic Polyether for Radiation Curing, in: *PRA Radcure Coatings and Inks*, Manchester, UK, 2002.
- [17] Miller, C.E. Hoyle, S. Jönsson, C. Nason, T.Y. Lee, W.F. Kuang, K. Viswanathan, N-Vinylamides and Reduction of Oxygen Inhibition in Photopolymerization of Simple Acrylate Formulations, *ACS Symposium Series*, 847 (2003) 2-14.
- [18] F. Morel, C. Decker, S. Jönsson, S.C. Clark, C.E. Hoyle, Kinetic study of the photo-induced copolymerization of N-substituted maleimides with electron donor monomers, *Polymer*, 40 (1999) 2447-2454.
- [19] C. Decker, D. Decker, Photoinitiated Polymerization of Vinyl Ether and Acrylate Monomer Mixtures, *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry*, 34 (1997) 605-625.
- [20] D. Leonhardt, D. Skinner, K. Kawamura, K. Ashikaga, D. Diehl, P.K. Swain, D. Harbourne, Advancements in UV LED technology and its impact on UV curing applications in: *RadTech Asia 2013*, Shanghai, 2013.
- [21] P. Esfandiari, S.C. Ligon, J.J. Lagref, R. Frantz, Z. Cherkaoui, R. Liska, Efficient stabilization of thiol-ene formulations in radical photopolymerization, *Journal of Polymer Science Part A: Polymer Chemistry*, 51 (2013) 4261-4266.