An Overview of Oxygen Inhibition in Photocuring

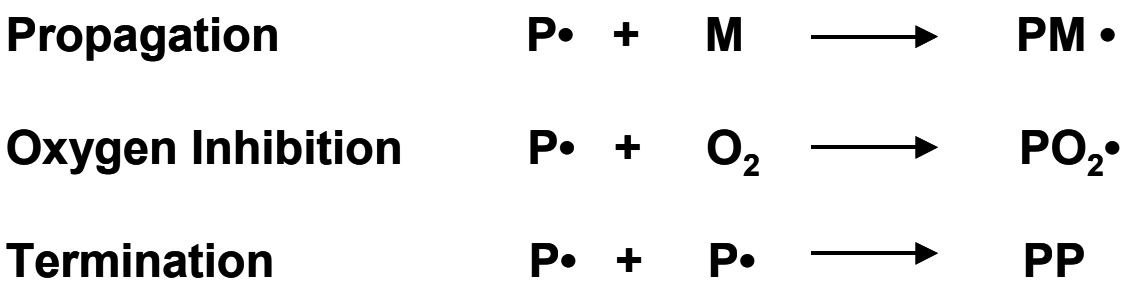
Charles E. Hoyle
School of Polymers and High Performance Materials
University of Southern Mississippi
Hattiesburg, MS 39406-0076

Abstract

It is well known that oxygen inhibits free-radical polymerization thereby reducing curing efficiency. Herein is described the physical and chemical methods of eliminating oxygen inhibition in radiation curing processes, or at least reducing its detrimental impact. This review is meant to serve as a starting point for developing strategy by formulators interested in minimizing oxygen inhibition in UV curable resins.

Introduction

Free-radical meth(acrylate) photopolymerization proceeds readily in nitrogen saturated samples to give highly crosslinked networks when the monomers are multifunctional.[1-5] Unfortunately, oxygen, which is present at a concentration of 10^{-2} to 10^{-3} M in most photocurable resins, inhibits free-radical polymerization according to Scheme I by reaction with carbon centered radicals in polymer chain ends results in chain termination. According to Scheme I, a growing polymer radical chain designated **P•** either adds to oxygen (inhibition), a monomer **M** (propagation), or another radical.



Scheme I. Propagation, Oxygen Inhibition, and Termination Steps in Free-Radical Polymerization.

Oxygen is particularly detrimental to chain propagation at the air-film interface since oxygen can continually diffuse into the interface and inhibit polymerization. Although oxygen inhibition must always be considered when formulating any photocurable resin, it is especially important in two cases: thin-film applications where oxygen can readily penetrate the entire bulk of the sample and highly filled (pigmented) systems where light penetration is significantly reduced. As with any problem, a large number of methods for overcoming oxygen inhibition in UV curing operations have been developed. We will review several methods for reducing oxygen inhibition, each of which has its own merits and shortcomings.

Discussion

Methods for overcoming oxygen inhibition can be divided into three convenient types: processing parameters, monomer structural features, and additives. The first includes some rather simple, but powerful, processing methods for reducing oxygen inhibition. The other two involve chemical structures of the monomers being polymerized or small molecule additives.

Processing Parameters

Inerting. The simplest method for overcoming oxygen inhibition is to inert the coating with a nitrogen blanket. Unfortunately, this is a costly solution to the problem and other methods that involve modification of the resin itself may be better choices in many cases.

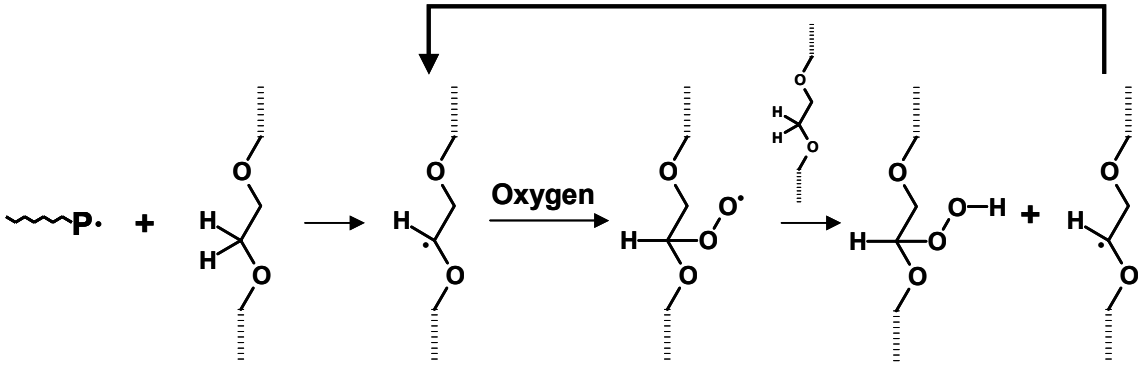
High Light Irradiance. Perhaps the most efficient method of overcoming oxygen inhibition in formulations which are particularly susceptible to oxygen inhibition is to use high light irradiance lamps.[6,7] This results in an immediate production of a high concentration of radical which react with oxygen, thus removing it from the coating. The use of high irradiance not only greatly reduces (one might say eliminates) the induction period associated with radical/oxygen reactions, but it also results in the rapid curing process required for many applications after the oxygen is eliminated. When considering the use of high irradiance sources it is essential to select a lamp with primary output in the region that the photoinitiator has its absorption maximum: this is especially important in pigmented formulations where there is a competition for the light by the pigment.

Physical barriers. Laminates or viscous chemical/physical barriers can be added to the resin to inhibit oxygen diffusion into the formulation.[8,9] Decker, et al.[8] commonly use thin films of polyethylene and/or polypropylene to sandwich the monomer sample such that within the time frame of the polymerization, the only oxygen inhibition that will result will be from oxygen initially dissolved in the liquid formulation.

Monomer Structural Features

In general, there are two monomers types which comprise the vast majority of photocuring applications: acrylates and methacrylates.[1-5] In typical photocuring applications, there are many important factors which must be considered when selecting a particular monomer or oligomer in a formulation ranging from resin rheological properties such as flow, leveling, etc. to how the structures alter the final physical and mechanical properties of the cured films.[3] In each case, the choice of the spacer group defines the type of chemical structural units that will make up the final cured film and will dictate the flexibility, hardness, adhesion, and gas permeability of the matrix. However, these groups can also alter the effectiveness of oxygen in inhibiting the polymerization. Higher viscosity monomers/oligomers limit oxygen diffusion and thus reduce oxygen inhibition. Certain chemical structures incorporated into monomers/oligomers greatly reduce oxygen inhibition by chemical processes which consume dissolved oxygen: the two most prominent chemical structures for reducing oxygen inhibition being ethylene or propylene glycol spacer groups and their thioether counterparts. The effect of the alkylene oxide (or sulfide) groups in minimizing oxygen inhibition is dramatic. Scheme II

presents a viable mechanism for the reduction in oxygen inhibition when alkylene oxide (or sulfide) repeat units are present in photocurable formulations.



.

Scheme II. Possible mechanism for reduction of oxygen inhibition in systems containing ethylene oxide groups.

The monomer functionality also reduces oxygen inhibition. Higher functional monomers produce highly crosslinked, microheterogeneous phase separated structures which prevent rapid oxygen diffusion. Monofunctional monomers greatly enhance the extent of oxygen inhibition in photocurable resin formulations by creating a loose network where oxygen diffusion occurs without hindrance. This is most easily demonstrated by photo-DSC peak maximum exotherm rate results in Figure 1 for photopolymerization of 1,6-hexanediol diacrylate (HDDA) samples with increasing concentration of hexyl acrylate (HA). The plot in Figure 1 is for the normalized ratio of the exotherm peak maximum of an HDDA sample in air in the absence of HA to the exotherm peak maxima of HDDA samples in the presence of HA at the concentration indicated. The decrease in exotherm rate maximum is substantial with increasing HA content. As already stated, addition of HA to HDDA increases oxygen diffusion to the growing polymer radical chain.

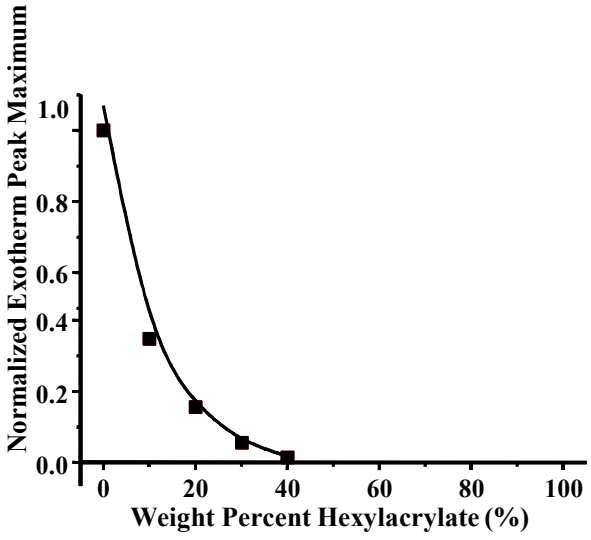


Figure 1. Normalized photo-DSC exotherm peak maxima for HDDA with added HA.

Additives

Photoinitiators. High concentrations of photoinitiator (greater than 5 weight percent in some cases) in photocurable formulations generate large radical concentrations that consume oxygen in the system and prevent further diffusion into the sample. By combining high photoinitiator concentrations with high irradiance, fast line speeds result.

Amines or N-Vinyl Amides. A rather simple method for reducing oxygen inhibition in radical polymerization is to add amines or N-vinyl amides to the formulation.[9,10] The general mechanism of oxygen scavenging by amines involves a radical chain process and has been described in several reports.[11-17] We note from practical experience in our lab that if very high irradiances and photoinitiator concentrations are used, the rate accelerating effect of amines is not significant. Cyclic N-vinyl amides such as N-vinyl pyrrolidone (NVP) and N-vinyl caprolactam (NVCL) have been used as reactive diluents and low viscosity modifiers for

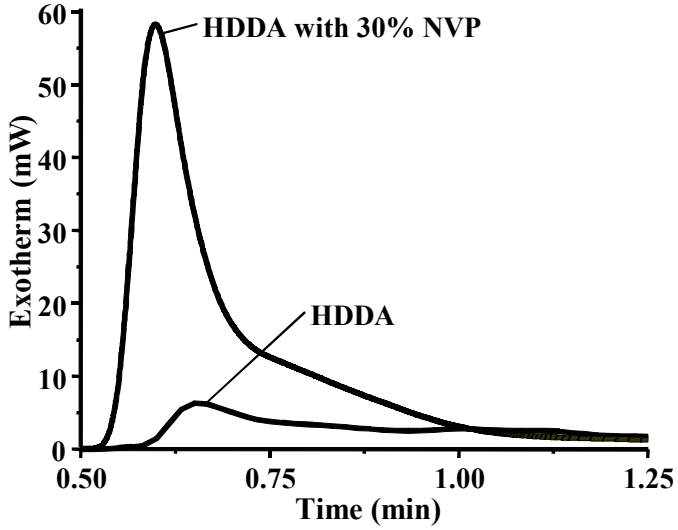


Figure 2. Photo-DSC exotherms of HDDA polymerization with 1 weight percent DMPA photoinitiator in air with and without added NVP.

photocurable formulations at levels of 2-30 weight percent.[18,19] They readily dissolve in almost all acrylates and reduce the effect of oxygen inhibition dramatically. Figure 2 shows photo-DSC exotherms of HDDA photopolymerization exotherms in air with and without 30 weight percent NVP. This result confirms reports[20, 21] that mixtures of NVP and HDDA exhibit unusually high rates of polymerization in air compared to either of the pure monomers under similar conditions. Several explanations have been proposed to account for the effect of N-vinyl amides in reducing oxygen inhibition. However, no clear mechanism has been substantiated to date. A detailed critique of the various mechanisms proposed for N-vinyl amide reduction of oxygen inhibition is given in two recent references.[22,23]

Phosphites and Phosphines. Tricovalent phosphite [($P(OR)_3$ or $P(OAr)_3$)] and phosphine (PR_3 or PAr_3) compounds commonly used as antioxidants[24] accelerate the rate of UV curing in air dramatically.[25,26,27] Quantitative results on the effect of two representative phosphorous compounds depicted are shown by photo-DSC results in Figure 3. As shown in Figure 3, addition of a relatively small amount of triethyl phosphite (TEP) is quite effective in increasing the rate of HDDA photopolymerization in air (curve a): note that the exotherm for HDDA in air without TEP is essentially on the baseline in Figure 3. In fact, the maximum polymerization rate is almost identical in nitrogen without TEP and air with TEP (see curves a and b).

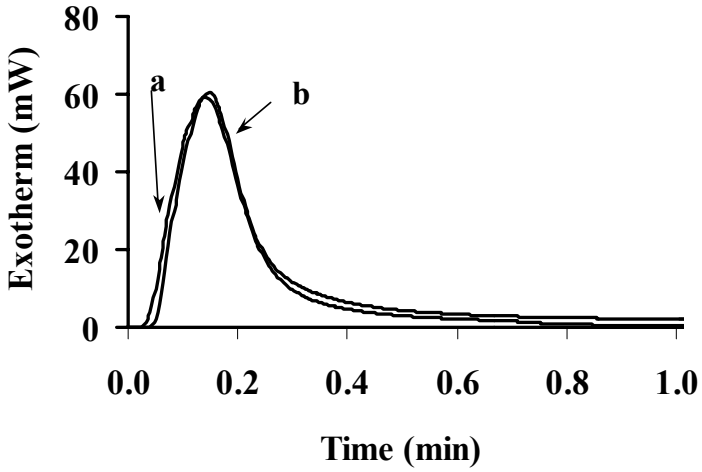


Figure 3. Photo-polymerization of HDDA with and without oxygen scavenger. Photoinitiator is 1 wt% DMPA; irradiance is 1.0 mW/cm^2. (a) HDDA with 1 wt% TEP in air, (b) HDDA in nitrogen.

The mechanism in Scheme III accounts for the efficient oxygen scavenging by alkyl phosphites in acrylate polymerization. Triarylphosphines also eliminates oxygen inhibition by a similar mechanism.

$$R\bullet + O_2 \longrightarrow ROO\bullet$$

$$ROO\bullet + P(OR`)_3 \longrightarrow O{=}P(OR`)_3 + RO\bullet$$

$$RO\bullet + P(OR`)_3 \longrightarrow R\bullet + O{=}P(OR`)_3$$

Scheme III. Phosphite oxygen scavenging mechanism.

Unfortunately the effectiveness of phosphites and phosphines diminishes rapidly with time after mixing: we have found that in some cases, the utility of phosphites and phosphines can be lost within 24 hours thereby limiting their use in many applications. A complete description of our results for various phosphites and phosphines is given in reference 28.

Thiols. Photocuring of equimolar thiol-ene mixtures proceeds rapidly in the presence of oxygen,[29] especially when thin samples are cured. The addition of thiols to conventional acrylate formulations can greatly reduce oxygen inhibition, and since thiols initiate acrylate polymerization there is no need to add photoinitiators. As shown in Figure 4, addition of 30 mol% of a conventional trifunctional thiol to HDDA with no added photoinitiator results in a polymerization rate that is rapid in both air and nitrogen. Comparable HDDA polymerization rates to those in Figure 4, but in air in the absence of thiol, can only be achieved with large photoinitiator concentrations and high light irradiances. Interestingly, the polymerization rate of a 30:70 molar thiol:acrylate sample in air with no added photoinitiator is markedly greater than for HDDA with a conventional photoinitiator in air! The mechanism proposed to account for the reduction in oxygen inhibition by addition of thiols is reproduced[30] in Scheme IV where RSH is a thiol group, RS• is a thiyl radical, CH_2=CHR is an acrylate group, and $PCH_2C^{\bullet}HR$ is the growing polymer radical.

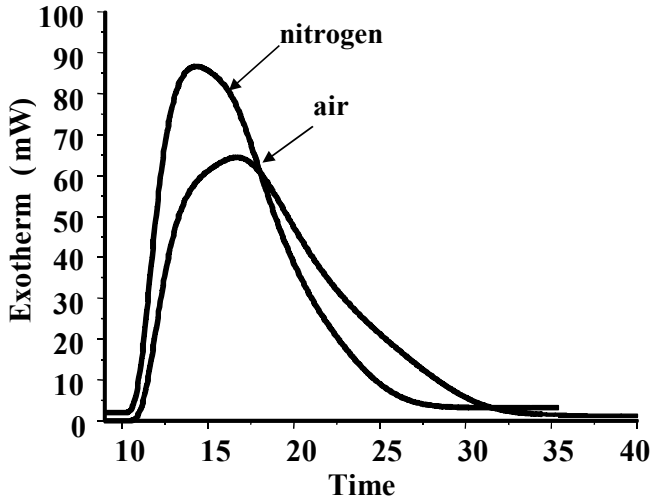
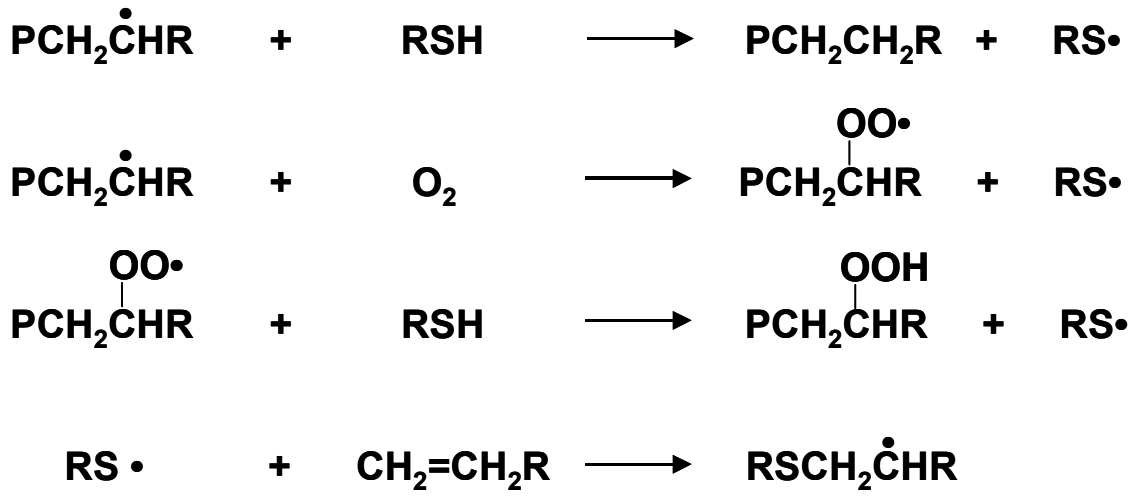


Figure 4. Photo-DSC exotherms of a 30:70 mole trithiol:HDDA mixture in air and nitrogen with no added photoinitiator.



Scheme IV. Thiol oxygen scavenging mechanism.

Conclusions

The problem of oxygen inhibition in photocuring processes can be tackled in a wide variety of ways ranging from processing strategies to the selection of reactive and non-reactive components. The requirements of the application will dictate which method or combination of methods must be used. The object of this review is to assemble all of the methods devised to date for overcoming oxygen inhibition into a concise reference with literature citations. Hopefully, this will provide the interested reader with a basic starting point for reducing oxygen inhibition.

Acknowledgements

We gratefully acknowledge the support of our work on photocuring from Fusion UV Systems, Inc., Albemarle Chemical Co., Ashland Chemical Co., the National Science Foundation, Becker-Acroma, Lockheed Martin, and Armstrong World Industries.

References

1. Fouassier, J.P, Photoinitiation, Photopolymerization and Photocuring; Verlag: New York, NY, (1995).
2. Radiation Curing: Science and Technology; Pappas, S.P.; Plenum Press: New York, NY, (1992).
3. Roffey, C.G., Photopolymerization of Surface Coatings, Wiley Interscience, NY, (1982).
4. Pappas, S.P. (ed.) "*UV Curing Science and Technology*", Plenum, NY, (1992).
5. J. P. Fouassier, Photoinitiation, Photopolymerization, Photocuring, Hanser, Munich, (1995).
6. Wight, F. R., J. Polymk. Sci.: Polym. Lett. Ed., 16, 121-127 (1978).
7. Decker, C., *Polym. Interntational* , **42**, 133-141 (1998).
8. Decker, C., and K. Moussa, *Macromolecules*, 22, 4455 (1989).

9. Selli, E. and I.R. Bellobono. "Photopolymerization of Multifunctional Monomers: Kinetic Aspects." in Radiation Curing in Polymer Science and Technology. Volume III: Polymerisation Mechanisms. J.P. Fouassier, and J.F. Rabek, editors. Elsevier Applied Science: London (1993).
10. Allen, N.S., M.A. Johnson, P.K.T. Oldring, M.S. Salim. Chemistry & Technology of UV & EB Formulation for Coatings, Inks & Paints. Volume 2: Prepolymers and Reactive Diluents for UV and EB Curable Formulations. P.K.T. Oldring, editor. SITA Technology: London (1991).
11. Decker, C. and Jenkins, A. D., *Macromolecules*, 18, 1241, (1985).
12. Cohen, S.G., A.Parola, and G.H. Parsons, *Chem. Reviews*, 73, 2, 141-161 (1973).
13. Bartholomew, R.F., and R.S. Davidson, *J. Chem. Soc. (C).*, 2342-2346 (1971).
14. Bartholomew, R.F., and R.S. Davidson, *J. Chem. Soc. (C).*, 2347-2351 (1971).
15. Schaefer, F.C., and W.D. Zimmerman, *J. Org. Chem.*, 35, 7, 2165-2174 (1970).
16. Morgan, C. R. and Kyle, David R., *J. Rad. Cur.*, 10(4), 4 (1983).
17. Hoyle, C. E. and Kim, K. J., *J. Rad. Cur.*, 12(4), 9 (1985).
18. Oldring, P.K.T. "Chapter 1: Introduction." in Chemistry & Technology of UV & EB Formulation for Coatings, Inks, & Paints. Volume 2: Prepolymers and Reactive Diluents for UV and EB Curable Formulations. P.K.T. Oldring, editor. SITA Technology: London (1991).
19. Dowbenko, R. et al., *Progress in Organic Coatings*, 11, 71-103 (1983).
20. Kloosterboer, J.G., G.J.M. Lippits, *Journal of Radiation Curing II*, 10 (1984).
21. Ors, J.A., et al. "Monomer Interaction: Effects of Polymer Cure." In Crosslinked Polymers: Chemistry, Properties and Applications. R. Dickie, S.S. Labana, and R.S. Bauer, Editors. Am. Chem. Soc. (1988).
22. Miller, C. W.; , Jönsson, S; Hoyle, C. E.; Yang, D.; Kuang, W.; Kess, R.; Iijima, T.; Nason, C.; Ng, L.-T., *Technical Proceedings: Radtech 2000,* 754 (2000).
23. Miller, C. W.; Viswanathan, K.;, Jönsson, S.; Nason, C.; Kuang, W.; Yang, D.; Kess, B.; Hoyle, C. , Polym. Prep.,
24. Schwetlick, K, *Pure and Applied Chemistry* 55, 1629 (1983).
25. Nakasuga, A., JP 01079213 (1989).
26. Schmitt, W., Purrmann, R., Jochum, P., DE 2811039 (1978).
27. Xiao, B., Zhou, Y., Li, S., Luo, M., Wang, X., Zhao, P., *Radiation Physics and Chemistry* 57, 421 (2000).
28. Kuang, W., Hoyle, C. E., Viswanathan, K., and Jönsson, S., Radtech North America 2002 Conf. Proc., 292 (2002).
29. Jacobine, A. T. Thiol-Ene Photopolymers in Radiation Curing in Polymer Science and Technology: Polymerization Mechanisms, Vol. III, eds, Fouassier, J. P.; Rabek, J. F., 1993, Elsevier Science Publishers Ltd., New York, pp. 219-268 (1993).
30. Gush, D. P.; Ketley, A. D., *Mod. Paint. Coat.*, 68, 61 (1978).