Photogenerated Amines as Novel Crosslinking Agents

D. Scott Bull
Corporate Research
National Starch and Chemical Company

Introduction

Reactive polyurethane-based coatings and adhesives are typically prepared by reacting polyether or polyester polyols with a stoichiometric excess of a di- or multifunctional isocyanate-containing compound. These prepolymers, or B-stage resins, then react with moisture in the substrates, the atmosphere, or both to complete the curing process (Figure 1).

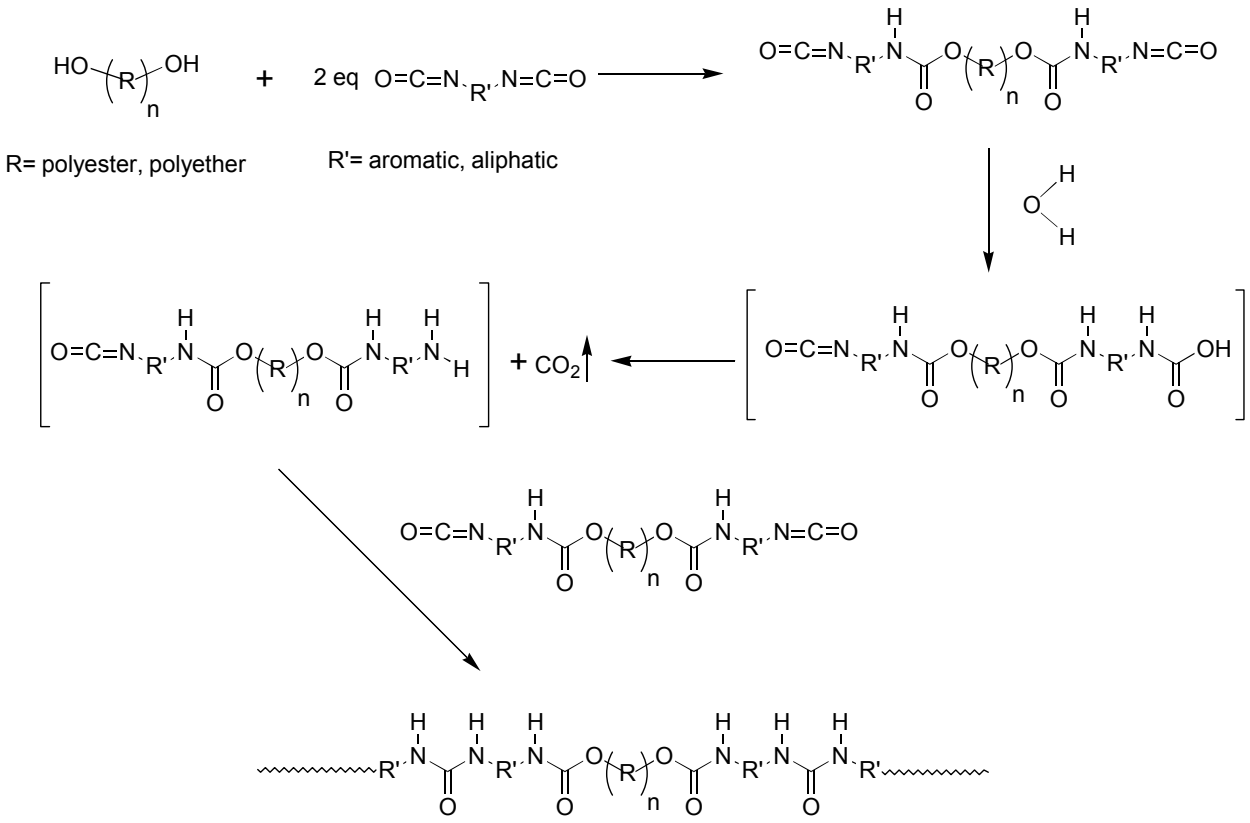


Figure 1. *Moisture Curing of Isocyanate-Based Formulations*

While the ultimate properties of these materials are quite good, the isocyanate/water reaction is relatively slow. In addition, hydrophobic formulation components and substrate geometry may limit diffusion of moisture to the reactive sites. These restrictions led us to search for latent curing agents that could, on demand, be activated by exposure to an energy source. Of the possible energy sources available, ultraviolet irradiation (UV) was chosen because it is rapid, cost effective, and currently being used on a production scale to cure other chemistries (i.e., acrylates, epoxies, etc.).

Our initial concept focussed on developing molecules that would decompose to form multifunctional nucleophiles upon exposure to UV irradiation. A review of the literature showed that amine[1], hydroxyl[2], and thiol[2] functionality had been generated by exposure of UV-labile precursors to UV irradiation. These methods were typically developed to provide protecting groups for the target functionality in multistep organic syntheses although the work of Nishikubo, *et al.* attempted to generate amines from arylformamides to cure epoxy and polyurethane oligomers.[1a]

Photogeneration of amines was chosen for our investigation due to the rapid reaction of isocyanates with amines, relative to hydroxyl or thiol functionalities.[3] Three reported approaches to generating amines looked promising from a synthetic standpoint. The first of these involved the photodecomposition of arylamides formed by the reaction of aryl isocyanates and carboxylic acids.[1a] The second approach, developed by Frechet, *et al*., involved the UV decomposition of 2-nitrobenzyl carbamates. The third method of generating amines via photodecomposition was reported by Chae and coworkers (Scheme 2).[1c] This group was interested in preparing amino-functional polymers in which the amines could subsequently be converted to diazo dye sites. Their goal was to produce a photoimagable polymer film by converting benzophenone oxime carbamates to the corresponding amine via exposure to UV irradiation. This amine-functional polymer was then diazotized to form dye sites only where irradiation had occurred. The amine monomer **3** was prepared by irradiating benzophenone oxime carbamate **2**, which was prepared in three steps from 4-maleimidobenzoic acid (**1**). This work was interesting for our purposes because the first two synthetic steps were conducted to generate isocyanate functionality *in-situ* via Curtius rearrangement. Therefore, we believed that benzophenone oxime carbamates of commercially available multifunctional isocyanates could be prepared as latent crosslinkers. After screening all three of these routes to photogenerated amines, we chose the oxime carbamate approach as the most interesting to pursue in terms of effectiveness, structure variation, and toxicity of byproducts.

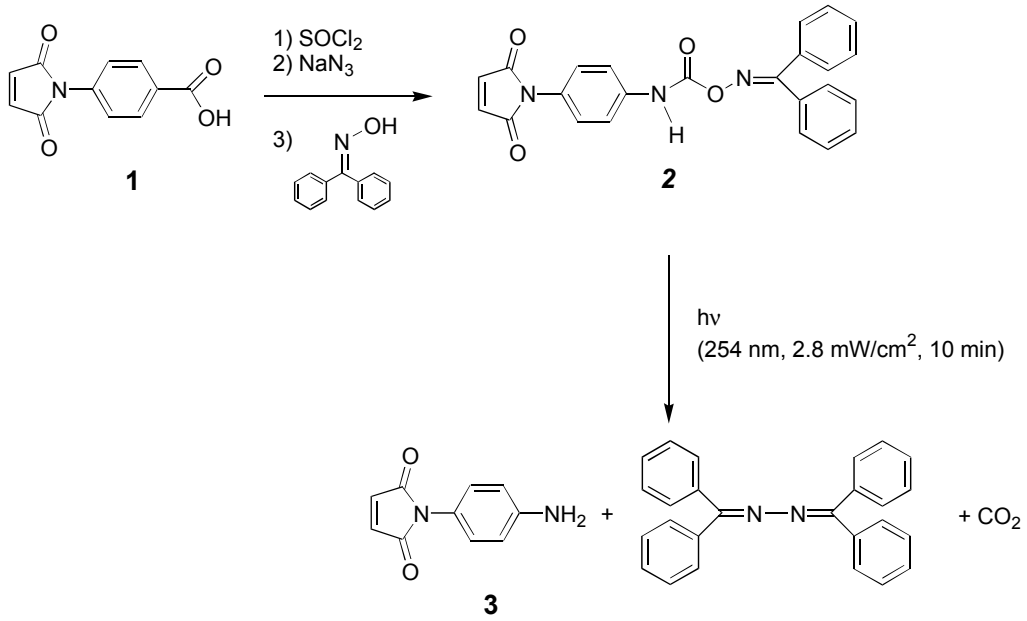


Figure 2. *Photogeneration of Amines from Benzophenone Oxime Carbamates*

Mechanistically, the conversion of oxime carbamate to the corresponding amine is as outlined in Figure 3. Initial absorbance of the UV-irradiation leads to homolytic cleavage of the nitrogen-oxygen bond. Decomposition of the resulting carbamate radical is driven by formation of carbon dioxide. The nitrogen-centered radical, formed by loss of CO_2 then abstracts a hydrogen to complete formation of the amine. In addition, tetraphenylazine is formed as a byproduct.

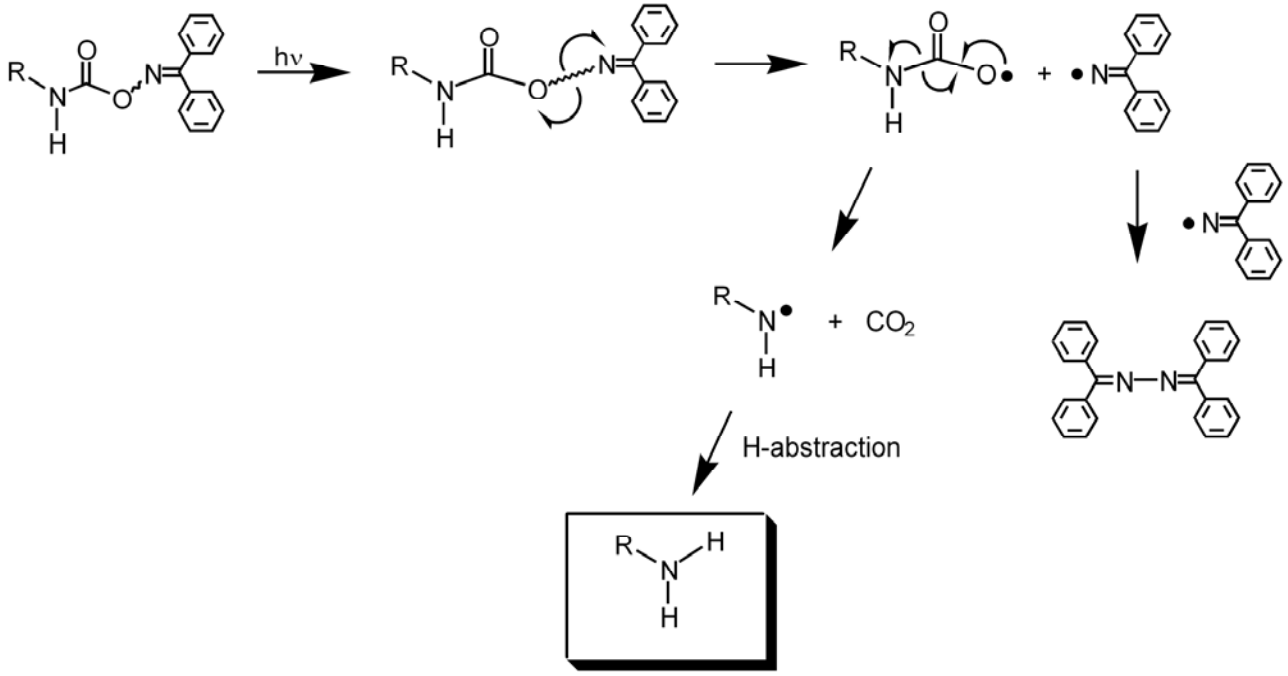


Figure 3. *Proposed Mechanism for Oxime Carbamate Photodecomposition*

Procedure

General

All reagents were used as received except where noted. Reagents were obtained from Sigma-Aldrich Chemical Company, except for the Desmodur® products, which were obtained from Bayer Corporation. Photoinitiators used as oxime substrates were provided by Chitec Chemical Company, Ltd., via Maroon and Campbell, Inc. Solvents were anhydrous grade except for toluene, which was dried over 5Å molecular sieves prior to use. Reactions involving isocyanates were typically conducted in oven-dried, multineck round bottom flasks fitted with a teflon/glass mechanical stirrer, thermometer, reflux condenser (if solvent was used), and inlet and outlet adapters for N_2 flow. N_2 was passed through Drierite prior to use.

Analytical

FT-IR spectra were obtained on KBr disks using a Nicolet Magna-IR 560 spectrometer, or a MIDAC M series real-time IR spectrometer. ^{1}H-NMR spectra were obtained on either a Varian DPX 400 MHz spectrometer, or a Bruker 300 MHz instrument using $CDCl_3$ or DMSO-d6 solvent. UV-Visible spectra were obtained in CH_3CN (0.1 mM) using a Perkin Elmer Lamda 20 UV/Vis spectrometer. Isocyanate titrations were conducted according to the procedure outlined in ASTM D2572-80.

Synthesis

Oximes: Oximes were prepared according to reported methods.[4] The actual method used was determined by product yield for each substrate. For our studies, the oximes were recrystallized from methanol and thoroughly dried prior to use in subsequent reactions.

Oxime Carbamates: Oxime carbamates were prepared by adding an equivalent molar amount of oxime to the isocyanate-containing compound which was previously dissolved in either anhydrous toluene or $CHCl_3$ under a blanket of dry N_2. The reaction was conducted at 60 °C until complete consumption of isocyanate functionality was indicated by IR spectroscopy. The product was then concentrated by rotary evaporator followed by Kugelrohr distillation (80 °C, 1-2 mm Hg).

Irradiation

Irradiations were conducted as noted using either a UVProcess® Supply, Inc. curing line equipped with a medium-pressure Hg bulb, or an EFOS Novacure® spot cure unit. The UVProcess line was operated at an intensity of 300 WPI and a belt speed of 12 FPM. This resulted in irradiation dosages of 1350, 1210, 194, and 750 mJ/cm^2 for UV-A, UV-B, UV-C, and UV-V spectral ranges, respectively. A typical irradiation procedure involved coating the material to be irradiated between two KBr IR plates, followed by irradiation through the plates. In the case of isocyanate-containing materials, the samples were prepared under dry N_2 and kept in a dessicator before and after irradiation.

Results and Discussion

The utility of using benzophenone oxime carbamates as UV-generated crosslinkers was examined by first preparing benzophenone oxime. Oxime carbamates were then formed from reaction with either di- or multifunctional isocyanates. For this initial study, we chose Desmodur W and Desmodur N-3400 as the isocyanate-functional substrates due to the fact that they would ultimately generate aliphatic amines, which are more reactive than aromatic amines toward isocyanates (Figure 4).

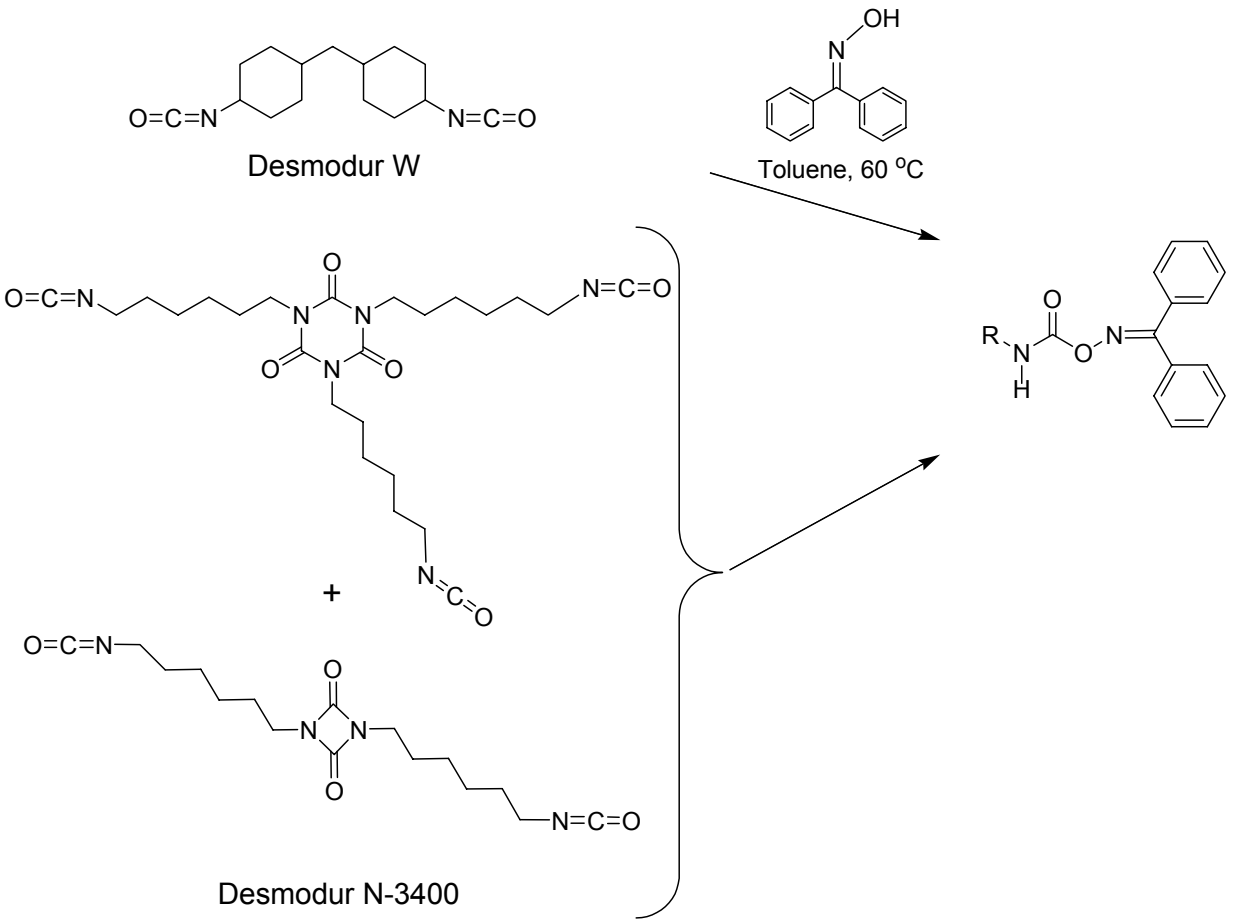


Figure 4. *Preparation of Benzophenone Oxime Carbamates From Commercial Aliphatic Isocyanates*

These oxime carbamates were analyzed by UV-Vis spectroscopy and found to have maximum absorbance in the 250-260 nm range with significant absorbance up to 300 nm. To confirm photodecomposition of these materials, films were cast from CH_2Cl_2 onto IR salt plates and irradiated on the UVProcess® Curing Line at a lamp setting of 300 WPI and a belt speed of 12 FPM with IR spectra taken before irradiation and after 1 and 10 passes. As shown in Figure 5, the desired photodecomposition of the Desmodur N-3400-based oxime carbamate was confirmed by the disappearance of the carbamate carbonyl absorbance (1742 cm^{-1}) as well as the appearance of the amine absorbance at 3355 cm^{-1}.

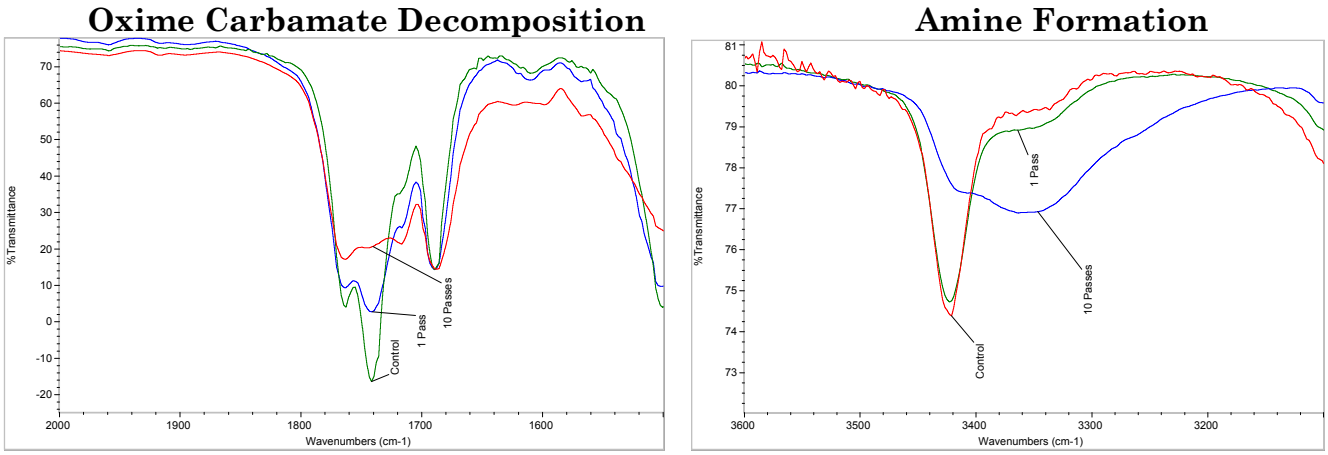


Figure 5. *Irradiation of Desmodur N-3400/Bis Benzophenone Oxime Carbamate (Oxime Carbamate Decomposition: 1742 cm^{-1}, Amine Formation: 3355 cm^{-1})*

Having confirmed the desired photochemical amine generation from these substrates, studies were then conducted to evaluate the curing of reactive polymers with these UV-generated crosslinkers. The first involved mixing the benzophenone oxime carbamates of Desmodur N-3400 and Desmodur W with a reactive hot melt adhesive (RHM) formulation containing residual isocyanate functionality. Our goal was to react these isocyanates with the amines generated by UV-decomposition of the benzophenone oxime carbamates. For this study, the crosslinkers were added at equivalent stoichiometric levels. Films of the RHM/crosslinker mixture were coated onto IR salt plates and irradiated using the UVProcess® curing line (medium pressure Hg lamp). Energy density was maximized by using the highest lamp setting (300 WPI) and the slowest belt speed (12 FPM). The actual energy density values were 1350 mJ/cm^2; 1200 mJ/cm^2; and 190 mJ/cm^2 in the UV-A, UV-B, and UV-C ranges, respectively. IR spectra were taken initially and after 1, 3, and 5 passes through the curing line. Relative efficiency was determined by observation of the isocyanate absorbance at 2270 cm^{-1}.

Figure 6 shows the reduction in isocyanate absorbance for formulations containing benzophenone oxime carbamates of either Desmodur W (W) or Desmodur N-3400 (N-3400) after the first pass through the curing line. The results show these benzophenone oxime carbamates to be effective curing agents and that the higher functionality of N-3400-based crosslinkers leads to improved curing relative to the purely difunctional Desmodur W-based compound.

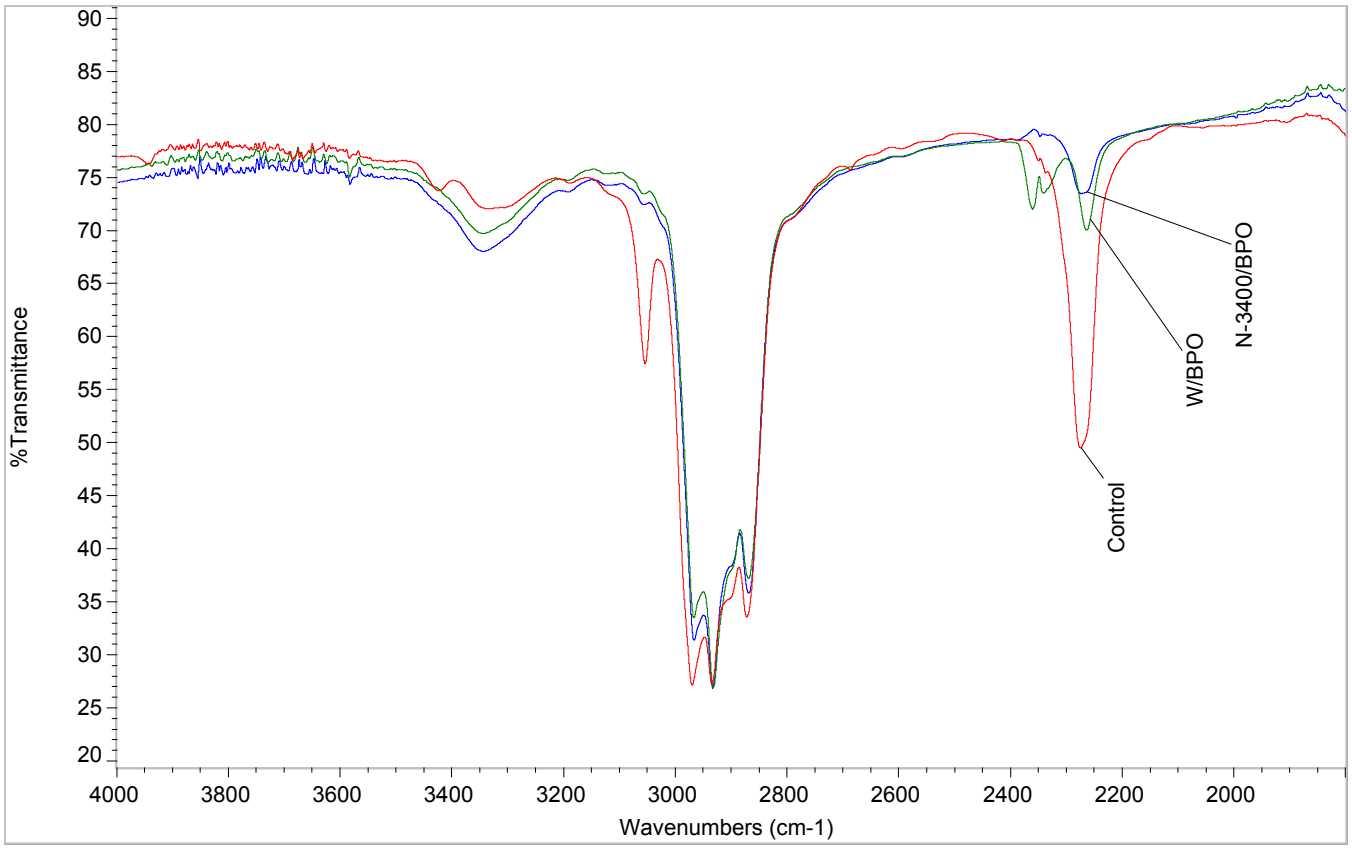


Figure 6. *Curing of RHM with UV-Generated Crosslinkers*

Having successfully demonstrated curing using benzophenone oxime carbamates prepared from commercial isocyanates, we decided to examine the concept of reacting a portion of the isocyanates present in prepolymers to obtain “internal” crosslinking sites. The internal crosslinker approach has several advantages over adding a separate crosslinking species. The main technical advantage is that each amine generated from the UV decomposition of an internal site leads to chain extension, where decomposition of both ends of a separate crosslinker species is required. Additional benefits include better formulation compatibility and reduced cost.

To test this hypothesis, we converted 50 mole% of the isocyanates present in a commercial reactive hot melt adhesive (RHM) formulation to benzophenone oxime carbamates in the usual manner. While the RHM is a highly formulated product, the reactive species is a prepolymer based on polyether/polyester glycols endcapped with methylene bis-diphenyl diisocyanate (Figure 7).

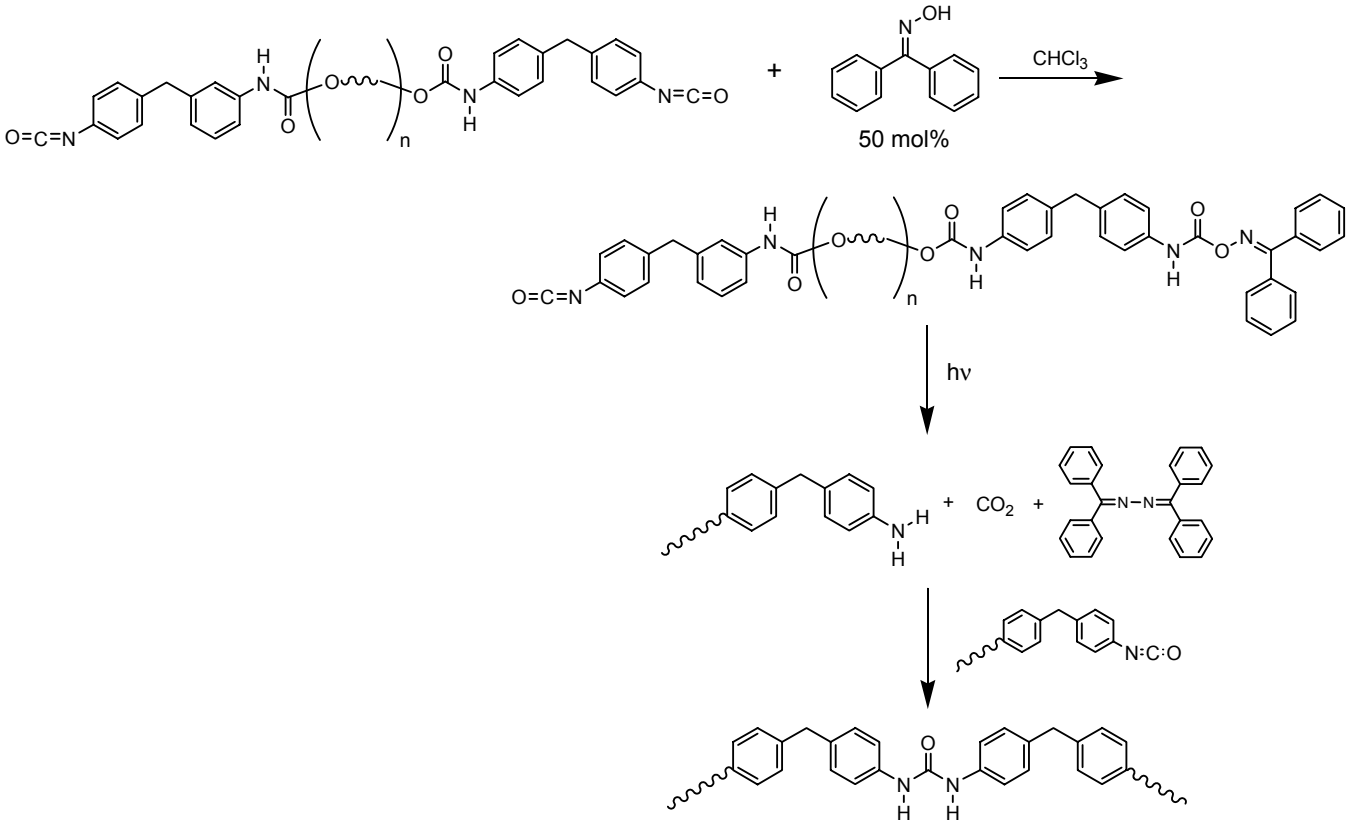


Figure 7. *Preparation and UV Curing of Reactive Hot Melt Adhesive with Internal Benzophenone Oxime Carbamates*

The curing efficacy of this derivatized formulation was determined by coating films between KBr plates and irradiating through the plates using the UVProcess® curing line as described previously. Reaction progress was monitored by FTIR spectroscopy by comparing samples that were irradiated for one and two passes through the curing line to an unirradiated control.

IR spectra of the three samples appear in Figure 8. The isocyanate absorbance at 2270 cm^{-1} has been dramatically reduced after one irradiation pass with only a slight reduction resulting from an additional pass. The residual isocyanate after one pass was < 3% of the unirradiated control. Therefore, the concept of incorporating an "internal" UV-generated amine precursor appears to be viable using benzophenone oxime methodology.

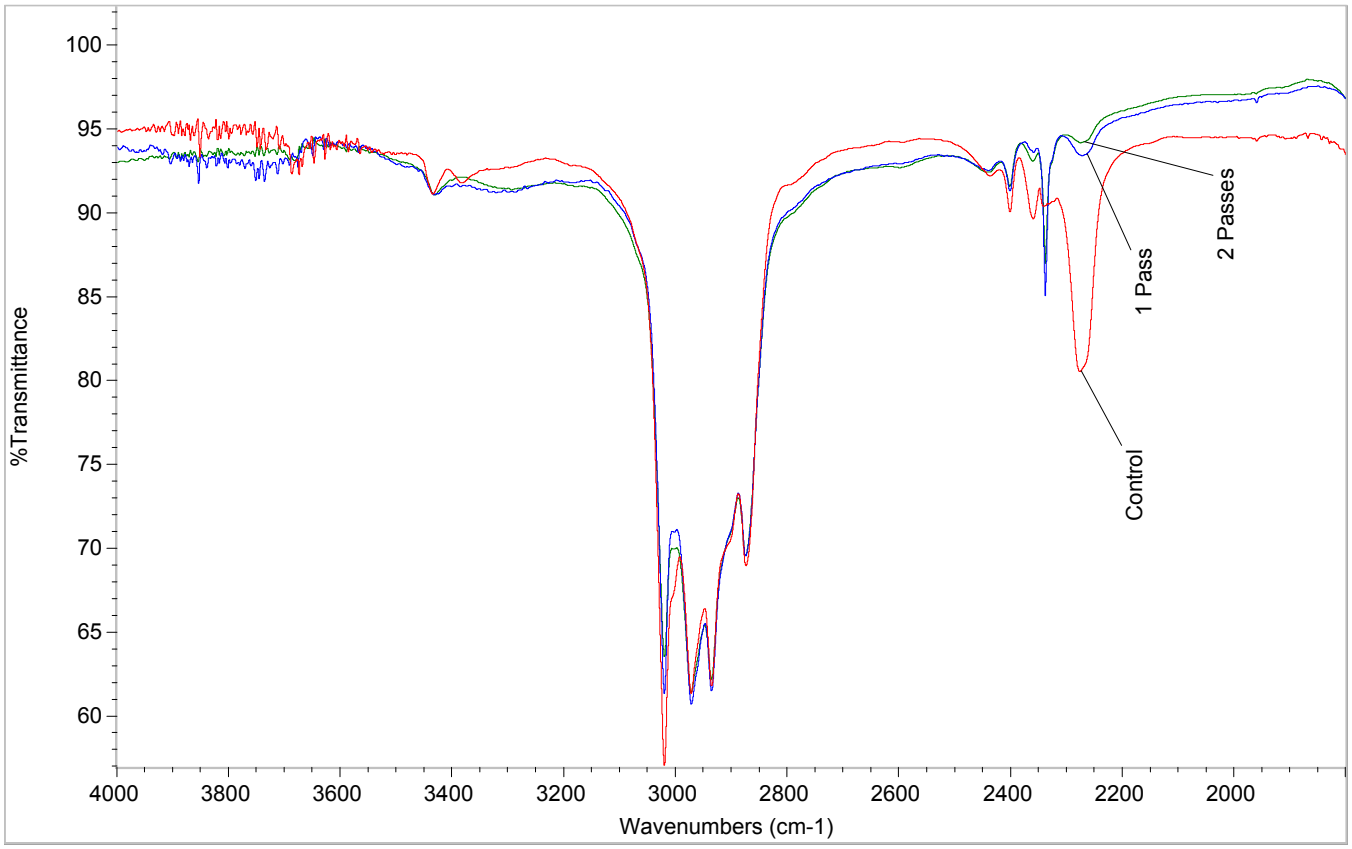
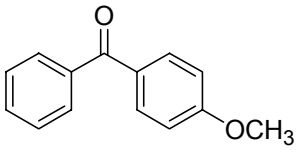
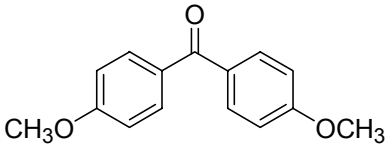


Figure 8. *Irradiation of RHM with "Internal" UV-Generated Amine Precursor*

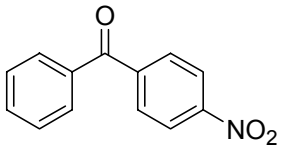
While the benzophenone oxime approach to photogenerated amines was successful, it was found to have a practical limitation in terms of cure depth. Films of about 1 mil thickness could be completely cured, but curing efficiency dropped dramatically at greater thickness. Our hypothesis is that beyond 1 mil, the absorbance of the aromatic rings from the MDI-based carbamates and/or the tetraphenyl azine byproduct outcompete the benzophenone chromophore for photons. We then focused our research on the development of chromophores with longer wavelength absorbance, which we hoped would lead to improvements in curing depth. To this end, we identified a variety of commercially available chromophores that potentially could be converted to the corresponding oximes and subsequently, oxime carbamates (Figure 9).



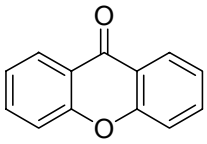
4-Methoxybenzophenone
λ=270 nm



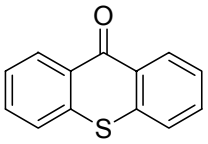
4,4'-Dimethoxybenzophenone
λ=273 nm



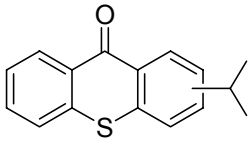
4-Nitrobenzophenone
λ=260 nm



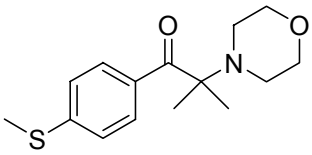
Xanthone
λ=250, 335 nm



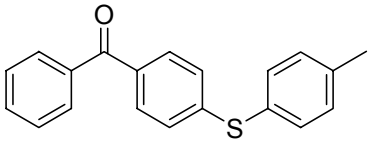
Thioxanthone
λ=255, 348 nm



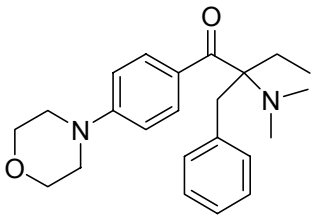
Isopropylthioxanthone
λ=250, 300, 385 nm



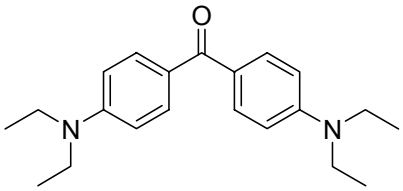
2-Methyl-1-[4-(methylthio)phenyl]-
2-morpholinopropan-1-one
λ=305 nm



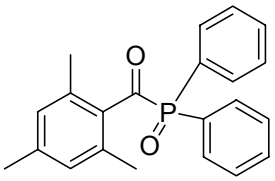
4-Benzoyl-4'-methyldiphenylsulfide
λ=246, 315 nm



2-Benzyl-2-(dimethylamino)-1-
[4-(4-morpholinoyl)phenyl]-1-butanone
λ=320 nm



N,N,N',N'-Tetraethyl-4,4'-diaminobenzophenone
λ=375 nm



2,4,6-Trimethylbenzoyldiphenylphosphine oxide
λ=246, 385 nm

Figure 9. *Commercial Photoinitiators as Potential Substrates for Conversion to Oximes*

Due to the different electronic environments around the carbonyl groups in each substrate, the efficiency of conversion to oxime differed substantially. Table 1 shows the isolated yields of oxime from each substrate. These results were obtained using the most effective preparative method for each substrate (*vide supra*).[4] Substrates containing morpholine rings were completely resistant to oxime conversion.

Table 1. *Conversion of Commercial Photoinitiators to the Corresponding Oxime*

Substrate		Oxime Conversion (%)
Benzophenone		99
4-Methoxybenzophenone		98
4,4'-Dimethoxybenzophenone		99
4-Nitrobenzophenone		90
4-Benzoyl-4'-methyldiphenylsulfide		88
Xanthone		61
Thioxanthone		24
Isopropylthioxanthone		*
N,N,N'N'-Tetraethyl-4,4'-diaminobenzophenone		*
2,4,6-Trimethylbenzoyldiphenyl phosphine oxide		*
2-Methyl-1-[4-methylthiophenyl]-2-morpholino-propan-1-one		No Reaction
2-Benzyl-1-dimethylamino-1-[4-morpholinophenyl]-butan-1-one		No Reaction

*Oxime formed, but recrystallization from methanol was not successful.

The oximes that could be prepared and isolated were screened for curing efficacy by first preparing the corresponding bis-oxime carbamates of hexamethylene diisocyanate (HDI). HDI was chosen since it was difunctional and because it was relatively easy to synthesize and characterize (Figure 10).

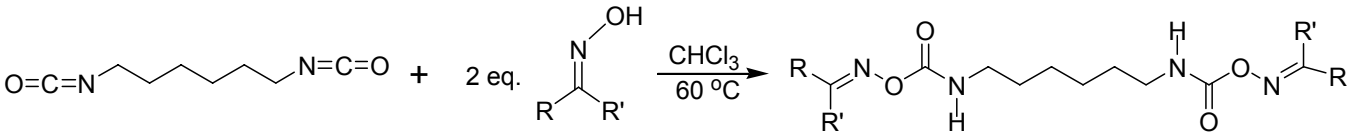


Figure 10. *Preparation of HDI-based UV-Generated Crosslinkers*

The curing effectiveness of these oximes was determined by curing a model reactive hot melt adhesive formulation with an equimolar amount of the corresponding HDI oxime carbamate. This initial screening showed that the highest degree of cure was obtained using benzophenone, 4-methoxybenzophenone, or 4-benzoyl-4'-methyldiphenylsulfide. These oximes were then used to prepare carbamates using 50% of the isocyanate functionality present in the reactive hot melt formulation. The oxime carbamate-modified RHMs were then cast between IR plates at 0.8 mil thickness and the plates were stacked to obtain a total thickness of 3 mils. After irradiation, the individual plates were analyzed by FTIR to determine the extent of cure for each layer. Figure 11 compares the residual isocyanate (peak at 2270 cm^{-1}) for each layer using either benzophenone or 4-methoxybenzophenone as the chromophore. By integrating these peaks and comparing them to integrals for the control samples, the percentage of curing could be calculated. The results of this analysis for benzophenone, 4-methoxybenzophenone, and 4-benzoyl-4'methyldiphenylsulfide are shown in Figure 12. This plot shows the extent of cure as a function of film thickness for all three chromophores. The greatest curing is obtained using 4-methoxybenzophenone, with benzophenone and 4-benzoyl-4'-methyldiphenylsulfide performing less effectively.

However, these data show that the practical thickness limit for curing using 4-methoxybenzophenone oxime carbamate is in the range of 1.5-2 mils.

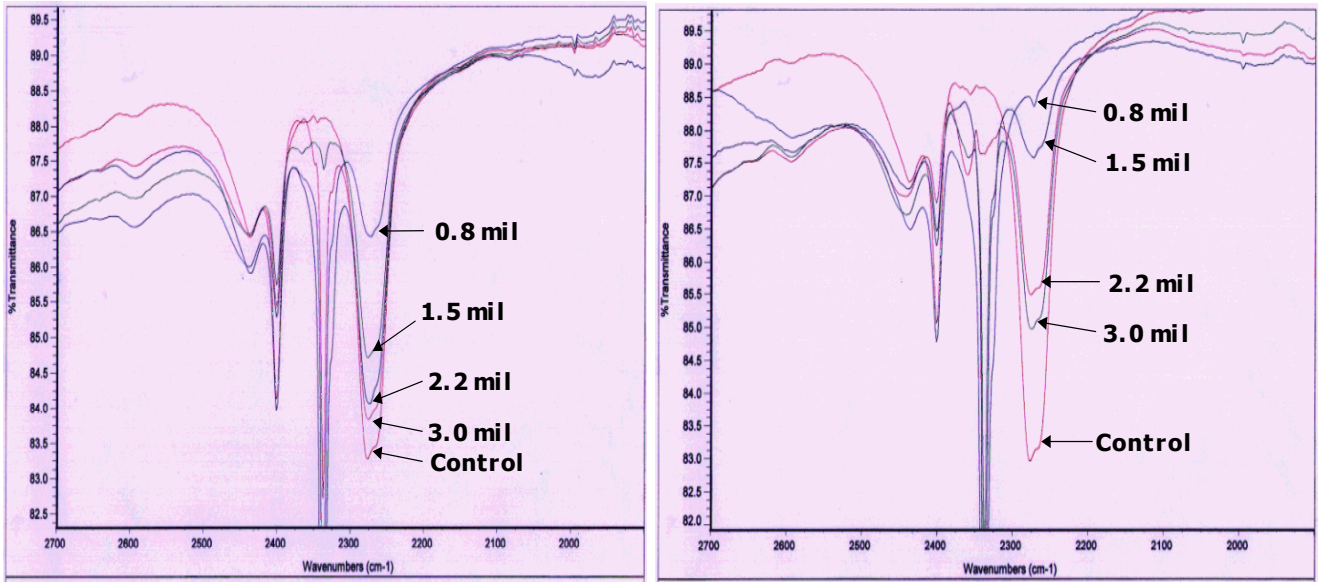


Figure 11. *UV Curing of RHM Modified with Benzophenone Oxime Carbamate (left) and 4-Methoxybenzophenone Oxime (right)*

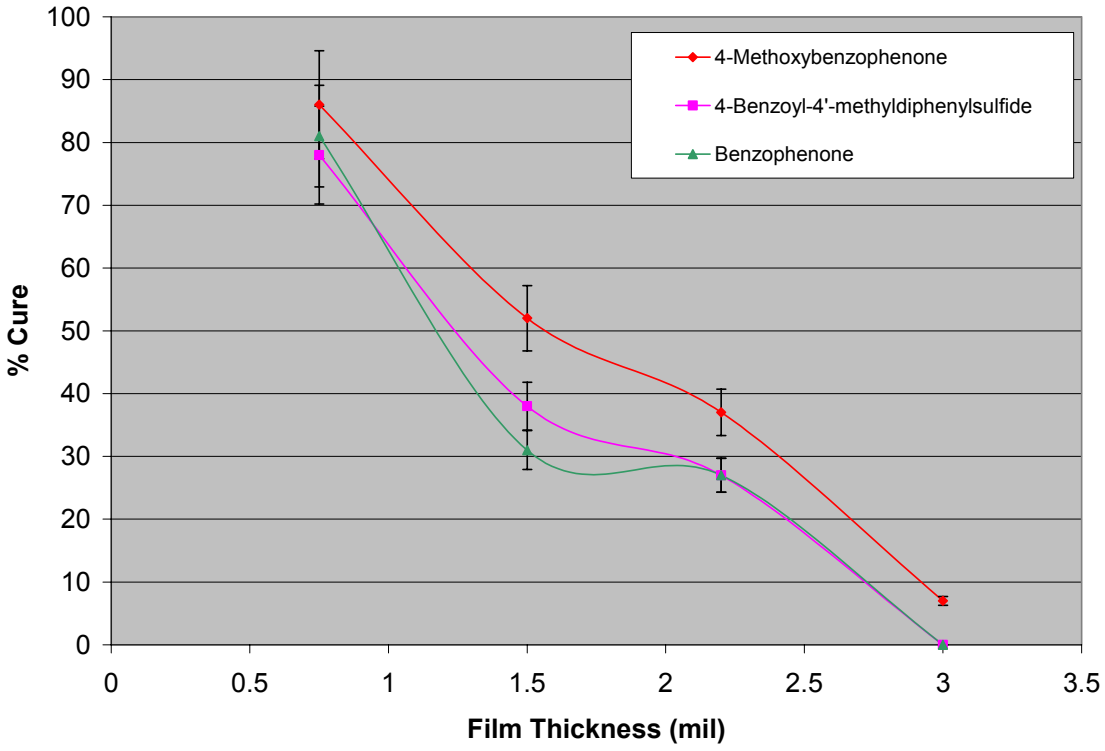


Figure 12. *Depth of Cure vs. Film Thickness for Reactive Hot Melt Formulation Modified with Oxime Carbamates*

Conclusions

Oxime carbamates have been reported to photolyze to the corresponding amine upon exposure to ultraviolet radiation. We have found that oxime carbamates based on multifunctional isocyanates can be used as photogenerated curing agents for isocyanate-functional formulations. In addition, oxime carbamates prepared directly on these isocyanate-functional prepolymers can be used to form integral amine functionality. Curing thickness can be influenced by the specific chromophore used, but is not directly correlated to the wavelength of absorbance. To date, this methodology is limited to relatively thin films.

Acknowledgements

The author would like to thank Wayne Chu, Don Herr, Bob Humphreys, and Nik Nikolic for their collaboration and helpful input into this program. In addition, special thanks go to Thad Campbell, of Campbell & Co. for providing samples of several commercial photoinitiators from Chitec Chemical Company, Ltd.

References

1. a. Nishikubo, T.; Takehara, E.; Kameyama, A. *Polym. J.* **1993**, *25(4*), 421-425.; Nishikubo, T.; Takehara, E.; Kameyama, A. J. *Polym. Sci: Pt.A: Polym.Chem*. **1993**, *31*, 3013-3020.

b. Cameron, J.F.; Frechet. J.M.J. *J. Am. Chem. Soc.* **1996,** *118*, 12925-12937.; Cameron, J.F.; Frechet. J.M.J. *J. Am. Chem. Soc.* **1991,** *113*, 4303-4313.

c. Chae, K.H.; Gwark, J.C.; Chang, T. *Macromol. Rapid Commun.* **2000**, *21*, 1007-1012; Chang, Y.C.; Kim, T.J.; Han, M.J.; Chae, K.H. *Polymer* **1999**, *40*, 4049-4054.

d. Ito, K.; Shigeru, Y.; Kawata, Y.; Ito, K.; Tsunooka, M. *Can. J. Chem.* **1995**, *73*, 1924-1932; Ito, K.; Nishimura, M.; Sashio, M.; Tsunooka, M. *J. Polym. Sci: Pt.A: Polym.Chem.* **1994**, *32*, 1793-1796, 2177-2185; Ito, K.; Nishimura, M.; Sashio, M.; Tsunooka, M. *Chem. Lett.* **1992**, 1153-1156.

e. Cossy, J.; Rakotoarisoa, H. *Tetrahedron Lett.* **2000**, *41*. 2097-2099.

f. Wang, B.; Zheng, A. *Chem. Pharm. Bull.* **1997**, *45(4)*, 715-718.

g. Corrie, J.; Papageorgiou, G. *J.C.S. Perkin 1*, **1996**, 1583-1592.

h. Church, G.; Ferland, J.-M.; Gauthier, J. *Tetrahedron Lett.* **1989**, *30(15),* 1901-1904.

i. Hamada, T.; Nishida, A.; Yonemitsu, O. *J. Am. Chem. Soc.* 1986, *108*, 140-145.

j. Pincock, J. A.; Jurgens, A. *Tetrahedron Lett.* **1979**, *12*, 1029-1030.

2. Jones, P.B.; Pollastri, M.P.; Porter, N.A. *J. Org. Chem*. **1996**, *61*, 9455-9461.

3. Szycher, M. “Szycher’s Handbook of Polyurethanes”, CRC Press, Boca Raton, 1999, **4**-20.

4. a. Lachman, A.; Noller, C.R. *Organic Syntheses*, Coll. Vol.2, Wiley, NY, 1943, 70-71.

b. Levine, A. W.; Fech, J*. J. Org. Chem*. **1972**, *37(10)*, 1500-1503.

c. Campbell, N.; McCallum, S.; Mackenzie, D.J. *J. Chem. Soc.* **1957**, 1922-1924.