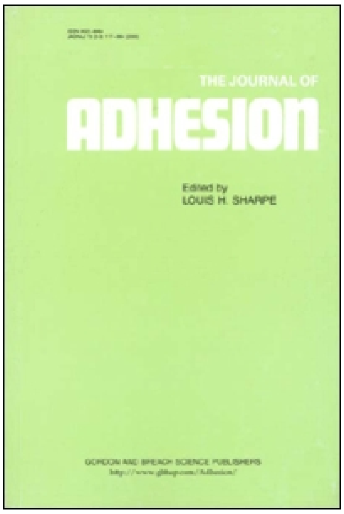

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# Characterization of Cure Profile of Anaerobic Adhesives by Real-Time FT-IR Spectroscopy. I. Effect of Transition Metal Dithiolate Complexes

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A model acrylic adhesive formulation consisting of triethylene glycol dimethacrylate (TRIEGMA) monomer, cumene hydroperoxide (CHP), o-benzoic sulfimide (saccharin or BS) and with or without a metal dithiolate catalyst has been made to study kinetics and mechanism of the anaerobic polymerization. In these studies, a real-time FT-IR spectroscopic (RT/FT-IR) technique has been used to study anaerobic cure profiles at room temperature. The catalytic effect of several transition metal dithio complexes for redox-initiated acrylate polymerization has been studied. The dithiolates used in these studies include the dithiocarbamate, xanthate dithiophosphate complexes of copper, nickel and zinc systems. Copper diacetylacetonate was also studied for comparison of its catalytic reactivity. A synergistic effect of copper dithiolate catalyst and saccharin was observed. The effects of catalyst concentration, metal and ligand type, and co-initiator on cure profiles have been monitored in a real-time mode.

KEY WORDS anaerobic adhesive; real time FT-IR spectroscopy; catalyst; dithiocarbamate; synergistic effect; xanthate; dithiophosphate; acrylate adhesive; degree of cure.

## INTRODUCTION

The cure profiles of anaerobic adhesives are of fundamental importance in adhesive design. Formulators are always interested in knowing the role each of the individual components of an adhesive play in the performance of that adhesive. Of particular concern is the effect of the catalyst and, if present, cure accelerator on cure speed and final cure performance. Historically, cure behavior of anaerobic adhesives has been evaluated by measuring the retaining and tensile shear strengths of the adhesives. Typically, these strengths have been determined by bonding metal parts with the adhesive and performing the appropriate test using a torque wrench or tensile-testing instrument, respectively. However, such a methodology of determining cure behavior is subjective and often inaccurate since bond strength relates not only to the degree of cure but also to various surface- and geometry-related parameters.

Real Time FT-IR (RT/FT-IR) spectroscopy has been recognized as a very sensitive tool for both quantitative and qualitative study of cure profiles for conversion of liquid monomers and oligomers to solid polymers.[1-6] For example, it has been shown that the RT/FT-IR technique can be used for monitoring fast radiation-induced anionic polymerization and metal-catalyzed hydrosilation reactions in a real-time mode.[1,2] The use of RT/FT-IR for anaerobic polymerization kinetic studies has also been reported.[5,6] Thus, the RT/FT-IR technique provides a non-destructive analytical method for monitoring the polymerization reaction at the molecular level, thus enabling easy detection of monomer residues, and the amounts present, in the cured products. The technique has proven to be quite sensitive to even small changes in monomer level and it provides good reproducibility of results. In general, this technique can be used for detecting levels of residual monomer(s) in any curable composition where the monomer(s) have characteristic absorption bands of high absorptivities (extinction coefficient) at frequencies where the polymer and any additives have negligible absorptions.

Typical anaerobic adhesives and sealants are one-part acrylic liquids which cure rapidly in the absence of oxygen, at or below room temperature. In the presence of oxygen, they can be stored for long periods of time, even at room temperature. From the dates of their discovery and commercialization, anaerobic adhesives and sealants have been the subject of many patents[7-17] and have found great success in a variety of industrial applications. Today, anaerobic adhesives or sealants are widely used for locking threaded assemblies, for sealing both threaded and flanged assemblies, and for assembling close-fitting (especially metal) parts. Over the years, anaerobic adhesive and sealant technology has advanced markedly with the most far-reaching advances being achieved by Loctite Corporation (Newington, Connecticut), the pioneer of this technology. For example, extensions of anaerobic adhesive chemistry have guided the development of impregnation of porous metal[18] which strengthens and improves the machinability of castings. Preapplied dry thread-locking and gasketing materials have improved the convenience and the durability of anaerobic structural adhesives. UV/anaerobic dual-cure systems provide the benefits of single-component, instant cure and high bonding strength adhesives for electronic assembly applications.[19,20]

Anaerobic formations cure through a redox-initiated, free-radical polymerization and comprise free radically curable monomers, especially acrylic esters; initiators, including initiator systems; stabilizers/inhibitors and modifiers and, depending upon the substrate, as discussed below, a catalyst. Typical initiator systems include those containing cumene hydroperoxide as the initiator in combination with an amine-functional reducing agent and an accelerator such as saccharin. As with most curable adhesives and sealants, optimization of a given formulation for a specific application is very much dependent upon cure speed. One parameter which greatly affects cure speed of anaerobic formulations is the presence of catalytic amounts of transition metals such as copper or iron. These metals enhance redox decomposition of the hydroperoxide initiator, thus speeding up cure initiation. Since anaerobic adhesives and sealants are most often used in bonding and sealing metal substrates, catalysts are typically provided through contact of the adhesive and sealant with the metallic substrate surface. Alternatively, such catalysts may be added to the anaerobic formulations themselves or applied to the substrates as a component of an accelerator/primer composition. The latter alternative is especially important where the substrates have inert surfaces and may be accomplished by spraying, dipping, or brushing the accelerator/primer composition onto the substrate surface prior to applying the anaerobic formulation. Several effective catalyst systems including dithiolate catalysts, have been reported in the patent literature.[12-17]

The present paper reports the results of our study on the effectiveness of transition metal dithiolate and other complex catalysts in anaerobic formulations using the RT/FT-IR technique. A discussion of the mechanism of anaerobic cure is also presented.

## EXPERIMENTAL

A model acrylic adhesive formulation consisting of triethyleneglycol dimethacrylate (TRIEGMA) monomer, cumene hydroperoxide (CHP) and o-benzoic sulfimide (saccharin or BS) was prepared for use in the present study. Formulations consisting of the model adhesive itself, *i.e.* without catalyst, as well as formulations with transition metal dithiolate or acetylacetonate catalysts were tested. The TRIEGMA monomer was obtained from Sartomer Company (West Chester, PA, USA) and CHP, BS, and copper diacetylacetonate were obtained from Aldrich (Milwaukee, WI, USA). The metal dithiocarbamate, tetraethylthiuram disulfide (ETHYL TUADS) and tetramethylthiuram monosulfide (UNADS) complexes were obtained from R. I. Vanderbilt Chemical (Norwalk, CT, USA). The nickel dithiophosphates were obtained from Custom Chem Lab (Livermore, CA, USA). The copper ethyl xanthate (copper bis-o-ethyl dithiocarbonate) was synthesized by reacting cupric chloride and sodium ethyl xanthate (obtained from TCI, Portland, OR, USA) in ethanol solution and precipitating the product out by the addition of water according to a published method.[21] All chemicals were used as received.

The model acrylic adhesive contained 2.64 wt% (or 2.75 vol%) of CHP, and 0.85 wt% of BS with the remainder being TRIEGMA monomer. The catalyst, when used, was employed in an amount of 0.35 wt%. The dissolution of BS and metal dithiolate catalysts in TRIEGMA monomer was assisted by using an ultrasonic bath. The addition of CHP initiator was always the last step before the formulations were to be tested. The formulations were not degassed prior to the reactions being carried out. The presence of oxygen is necessary to stabilize the anaerobic formulations. Dissolved oxygen in the formulation prevents premature curing. The oxidation and oxygen absorption of the acrylate monomers in anaerobic adhesives has been studied[22] and it was found that different additives may produce a different degree of oxygen absorption. However, at room temperature and within the time frame of our experiments, the solubility of the oxygen in the monomer is considered a constant. Therefore, the dissolved oxygen in the formulation was not treated as one of the major factors affecting the reaction kinetics in our experiments.

All RT/FT-IR kinetic runs of anaerobic curable samples were carried out using a Bio-Rad (Cambridge, MA, USA) FTS-60 system with a MCT detector on samples having a film thickness of 30–50 microns, coated on a sodium chloride disc. The adhesive-coated disc was then placed against a reflective surface of an aluminum

2024 alloy plate containing about 4 to 5 wt% of copper. An anaerobic environment for curing the adhesive was created by placing the salt disc and the aluminum plate in close contact, thus essentially eliminating contact of the adhesive with air. The aluminum surface was cleaned by immersion in methanol before it was used. The aluminum plate was positioned on a Harrick Retro-Mirror and Focus Transfer Accessory (Ossining, NY, USA) for External Absorption-Reflection IR spectral measurements. Spectra were recorded at 8 $\mathrm{cm}^{-1}$ resolution. A computer program was written, incorporating Digilab's GC/FT-IR software, for kinetic data acquisition and manipulation. A detailed description of this methodology has previously been given.[1]

## REAL-TIME FT-IR (RT/FT-IR) SPECTROSCOPY

The principle for using real time FT-IR techniques for polymerization kinetics studies is based on its ability to monitor directly the change in chemical structure of the components in the formulations during polymerization. Thus, the decrease of monomer, or increase of polymer, as a function of reaction time can be recorded spectroscopically. For anaerobic formulations comprised of acrylic monomer, the concentration of vinyl double bonds remaining in the samples before and after the reaction is shown by the decrease in intensity of the peak at 1634 $\mathrm{cm}^{-1}$, referring to the C=C stretching of the vinyl group, or 810 $\mathrm{cm}^{-1}$ referring to the C—H deformation mode of the vinyl group. Therefore, the degree of cure and cure rate can be determined from spectral change measurements at these frequencies. This information provides a quantitative analysis of the cure kinetics parameters, such as reactivities of initiators, resins or stabilizers, and induction or post-cure periods. It may also be used to determine the amount of the residual monomer in the cured polymer.

The degree of cure of the acrylate adhesives may be expressed as below:

$$\text{Degree of Cure} = \frac{A_o - A_t}{A_o} \tag{1}$$

Where $A_o$ = the ratio of the area of the peak between 1650 and 1610 $\mathrm{cm}^{-1}$ and the area of the peak between 1780 and 1660 $\mathrm{cm}^{-1}$ at time zero; and $A_t$ = the ratio of the area of the same two peaks at time t.

The rate of polymerization ($R_p$) is given by:

$$R_p = \frac{[M]\,(A_{t1} - A_{t2})}{(t_2 - t_1) \times A_o} \tag{2}$$

Where $A_o$, $A_{t1}$, $A_{t2}$ are the area ratios of peaks described above at times $t_o$, $t_1$, $t_2$, respectively. M is the original concentration of acrylic double bonds of the monomer used. The RT/FT-IR technique monitors the entire spectrum using an unchanged reference peak as an internal standard. Thus, it provides better accuracy and more reproducible kinetic measurements compared with the published method described by Decker *et al.*[23,24] which uses a dispersive infrared spectrometer for monitoring the peak height of a vinyl peak at a single wavelength. This is because when the monomer is converted to the polymer, some interferences by other components in the formulation may occur due to absorption in the same region or by inter-molecular interaction, such as hydrogen bonding, or by intra-molecular structural change, such as the loss of conjugation of related functional groups,[6,25] and frequency shifts and intensity changes may develop. The determination of the area under the absorption bands will be less sensitive to the frequency shift than the absorption maximum measurement, especially when the band to be monitored is a narrow band. It is reasonable to expect that current studies using the integrated absorption area will reduce experimental deviation.

Figure 1 shows a typical example of a stacked plot of IR spectra for the anaerobic polymerization of triethyleneglycol dimethacrylate (TRIEGMA) monomer over a 120-minute reaction time period. Since this is a relatively slow reaction, as compared with a photo cure reaction, the spectra were collected every five minutes during the two-hour reaction period. As shown in this figure, the speed of disappearance of the 1634 cm$^{-1}$ peak as a function of time represents the rate of consumption of the TRIEGMA monomer. The carbonyl peak at 1730 cm$^{-1}$ was used as an internal standard peak for all kinetic calculations. The slight shift of this carbonyl peak is due to loss of conjugation of the carbonyl bond and the C=C bond in the uncured state, as discussed in the literature.[6,25]

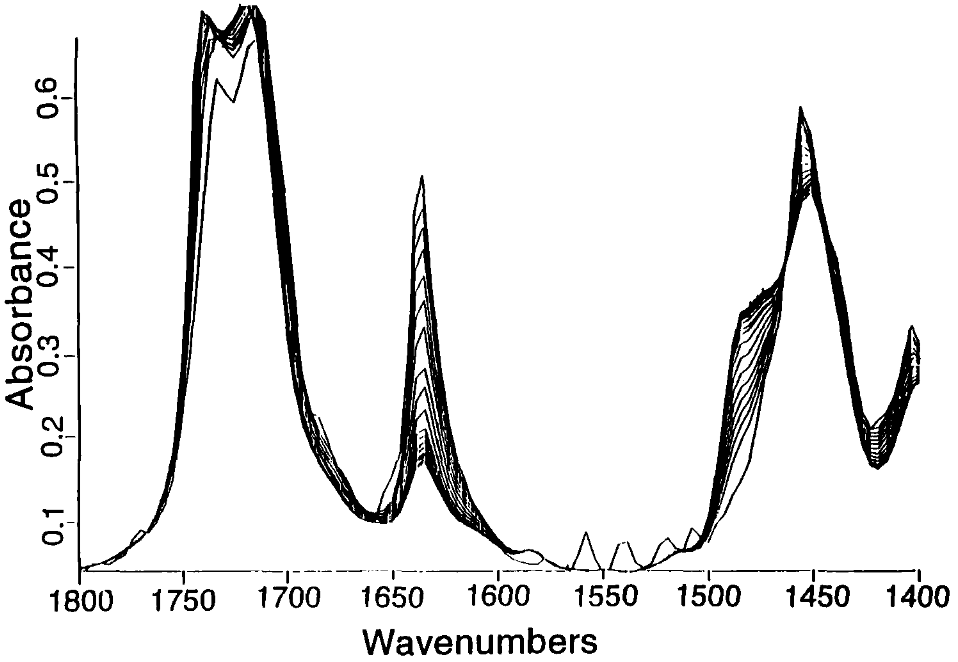


FIGURE 1 Typical RT/FT-IR spectral stack plot, for model anaerobic methacrylate adhesive on aluminum 2024 surface, in the 1400–1800 cm$^{-1}$ region. The time interval is 15 minutes. Example of decrease in the 1634 cm$^{-1}$ of C=C band is monitored.[6]

## RESULTS

Dithiolate salts exist as neutral complexes in which the metal ion is tightly associated with the dithiolate functional group until decomposition or reaction during the redox cycle of polymerization initiation. The manipulation of the organo group can easily be performed to improve solubility of the salt in an organic solvent or a particular monomer system. For instance, dibenzyldithiocarbamates are more soluble in (meth)acrylate capped ethoxylated bisphenol A than are dibutyldithiocarbamates. Thus, proper choice of alkyl chain length gives the dithiolate salts good solubility in anaerobic adhesive systems.

### A. The Effect of Metal Dithiolate Catalyst Concentration

The effect of metal concentration on cure profile is shown in Figure 2. Specifically, a copper dimethyldithiocarbamate (Cu-DMDTC) in an amount of 0.35 wt% (composition A) and 0.70 wt% (composition B) was added to the base adhesive (composition C) which comprised 0.85 wt% of BS and 2.64 wt% (or 2.75 vol%) of CHP in TRIEGMA monomer. For comparative purposes, cure of the base adhesive

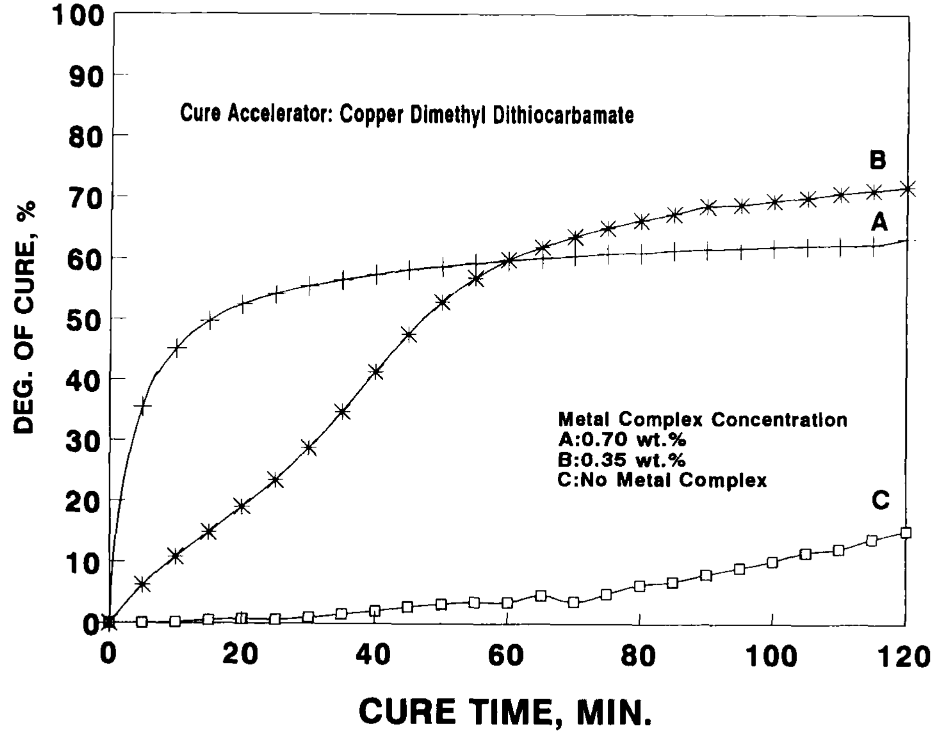


FIGURE 2 Plot of percentage cure *vs.* time of reaction for model anaerobic adhesive on the aluminum surface with the following concentrations of Cu-DMDTC catalyst: A: no metal catalyst; B: with 0.35 wt%; C: with 0.70 wt%.

(composition C) without catalyst was also monitored. Figure 2 illustrates that in the presence of copper dimethyldithiocarbamate catalyst, the cure rate can be enhanced. Thus, a degree of cure of more than 60% can be obtained after two hours in the presence of catalyst, as compared with only about 15% without the catalyst. Also, the cure acceleration is dependent on the catalyst concentration. As shown in Figure 2, a rapid initial cure acceleration and, ultimately, lower final degree of cure was observed when higher concentrations of copper catalyst were used.

### B. The Effect of Co-initiator

The results of the studies of the effect of saccharin co-initiator are shown in Figure 3. A base composition (composition A), free of BS co-accelerator, was prepared by adding 2.64 wt% (or 2.75 vol%) CHP to the TRIEGMA monomer. Three additional formulations were prepared by adding 0.35 wt% Cu-DMDTC (composition B); 0.35 wt% Cu-DMDTC and 0.85 wt% BS (composition C); and 0.85 wt% BS (composition D) to the base formulation. Figure 3 illustrates the cure rate against time for compositions A, B, C and D. From Figure 3 it is apparent that a sulfimide type co-accelerator is necessary to obtain any significant acceleration with the dithio-

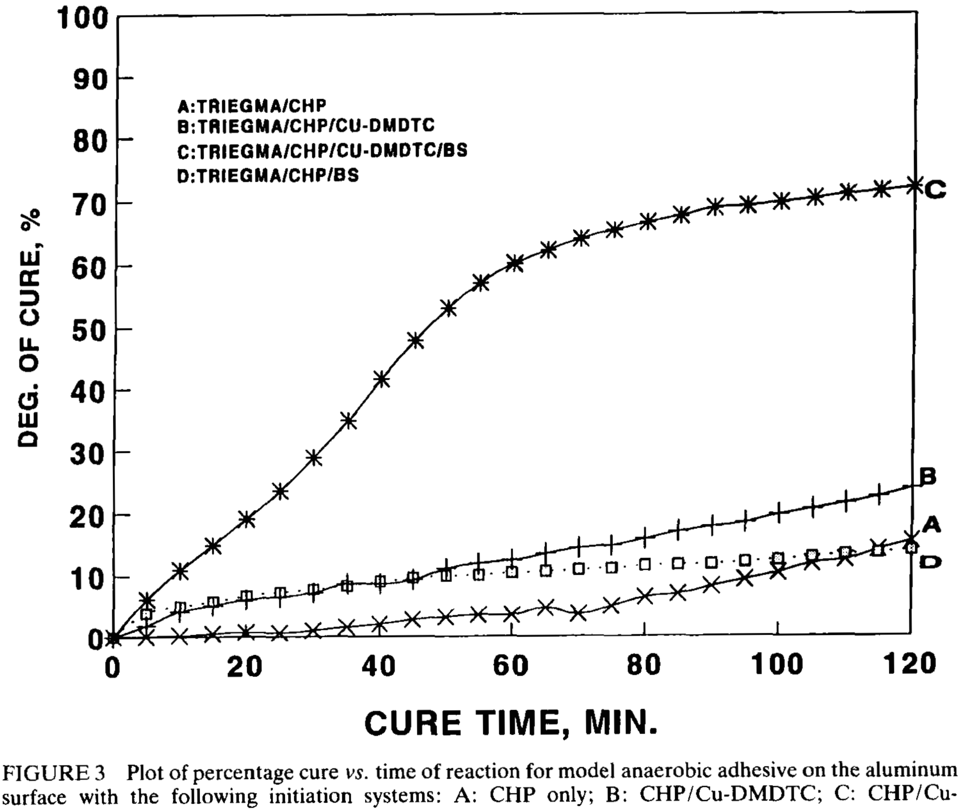


FIGURE 3 Plot of percentage cure *vs.* time of reaction for model anaerobic adhesive on the aluminum surface with the following initiation systems: A: CHP only; B: CHP/Cu-DMDTC; C: CHP/Cu-DMDTC/BS; D: CHP/BS.

late salt compound. Whereas neither the metal catalyst nor the saccharin alone, in base composition A, shows significant acceleration effect, the combination of BS and copper dithiocarbamate give a synergistic effect on cure acceleration. The mechanism of this synergistic effect on anaerobic cure is still not clear.

### C. The Effect of Transition Metal Type

The results of the studies on the catalytic cure acceleration effect of zinc, nickel and copper dithiocarbamate in a TRIEGMA/CHP/BS system are shown in Figure 4. In these systems, the ligand type of metal dithiocarbamate complexes is very similar. These results clearly demonstrate that the order of catalytic activity of the metal is Cu>NI≫Zn and it appears to be related to the redox potential for these metals in various oxidation states.

### D. Effect of Ligand

Various copper and nickel dithiolate complexes were added to the base formulation (formulation G). The metal dithiolates tested include copper complexes of diacetyl-

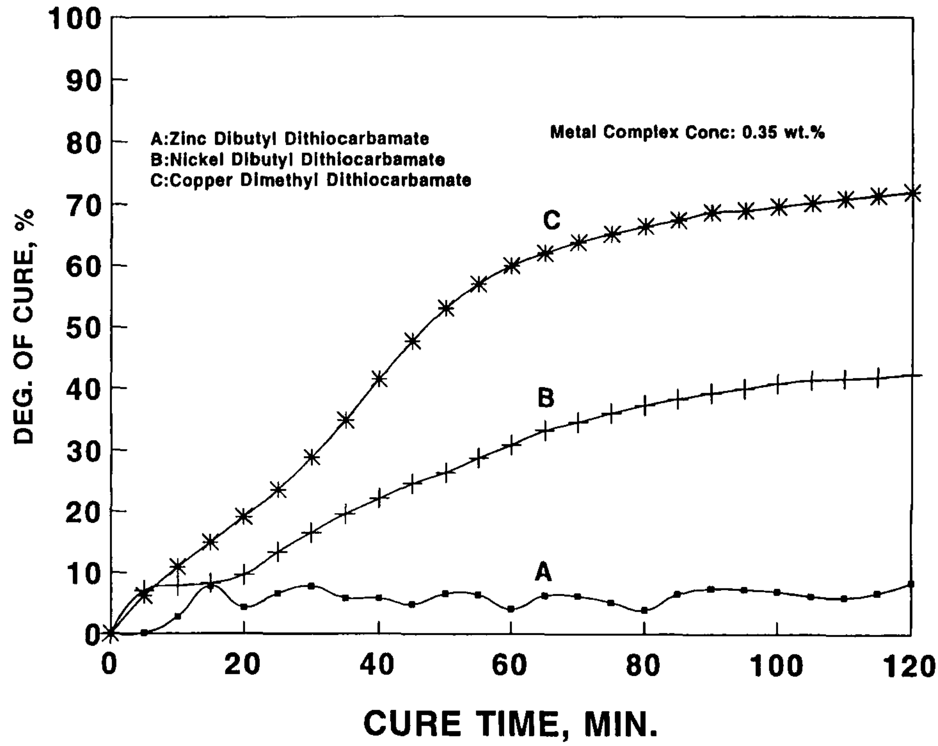


FIGURE 4 Plot of percentage cure *vs.* time of reaction for model anaerobic adhesive on the aluminum surface with the following metal dithiocarbamates: A: zinc dibutyl dithiocarbamate; B: nickel dibutyldithiocarbamate; C: copper dimethyldithiocarbamate.

acetonate (formulation A), ethyl xanthate (formulation B), dimethyl dithiocarbamate (formulation C), bis-2-hydroxyl-ethyl dithiocarbamate (formulation D), and nickel complexes of dibutyldithiocarbamate (formulation E) and dioctadecyl dithiophosphate (formulation F). As can be seen from Figure 5, compositions B, C and D all gave significant cure acceleration relative to the base composition G. The catalytic effect of the copper dithiolates varied only slightly during the first hour of cure as the ligand type changed. However, of the three copper-dithiolate-containing compositions, the copper xanthate appears to give the most active property for cure acceleration. For nickel dithiolates, the dithiophosphate form appears to be more active than in the dithiocarbamate form. The copper diacetylacetonate appears to be less active than the copper dithiolate complexes but, over time, more active than the nickel dithiolate catalysts. Specifically, the curves for compositions A and E in Figure 5 reveal that during the first hour of cure the copper diacetylacetonate does not show significantly more activity than the nickel dithiolates; however, after two hours it reached a much higher final degree of cure. This observation may be due to the initial decomposition rate of the copper diacetylacetonate which was slower than the nickel dithiolate complex.

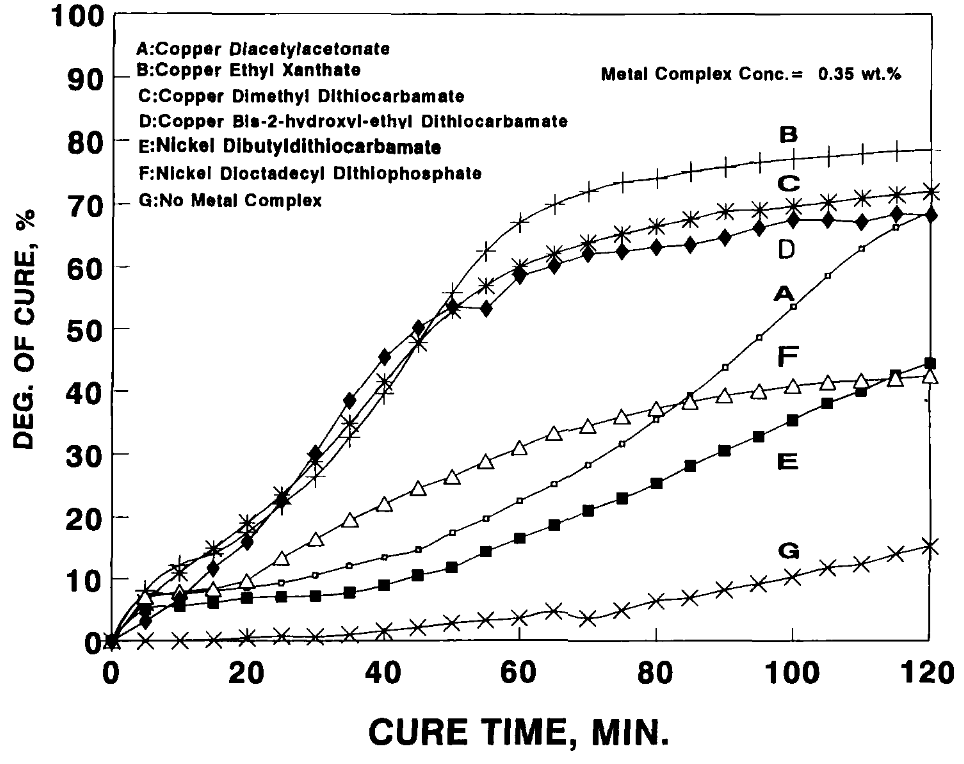
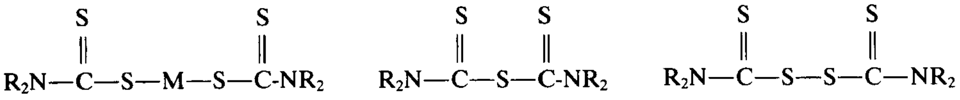


FIGURE 5 Plot of percentage cure *vs.* time of reaction for model anaerobic adhesive on the aluminum surface with the following transition metal catalysts: A: copper diacetylacetonate; B: copper ethyl xanthate; C: copper dimethyldithiocarbamate; D: copper bis-2-hydroxyethyl dithiocarbamate; E: nickel dibutyldithiocarbamate; F: nickel dioctadecyl diphosphate; G: no catalysts.



$R_2N-\overset{S}{\overset{\|}{C}}-S-M-S-\overset{S}{\overset{\|}{C}}-NR_2 \qquad R_2N-\overset{S}{\overset{\|}{C}}-S-\overset{S}{\overset{\|}{C}}-NR_2 \qquad R_2N-\overset{S}{\overset{\|}{C}}-S-S-\overset{S}{\overset{\|}{C}}-NR_2$

Where M = Cu, Ni, Zn, etc., R = alkyl

FIGURE 6 Chemical Structures of metal dithiocarbamate, tetraalkylthiuram mono- and di-sulfides.

### E. The Effect of Transition Metal in Dithiolates

In order to examine the importance of transition metal in the dithiolate complexes for cure acceleration of anaerobic adhesives and sealants, investigations were carried out to compare the cure acceleration activities of copper dimethyldithiocarbamate (Cu-DMDTC), tetramethylthiuram monosulfide (UNADS) and tetraethylthiuram disulfide (EtTUADS) in anaerobic formulations. The chemical structure of these three types of thio containing compounds are shown in Figure 6. Thus, these three types of compounds have a very similar $R_2N\text{-}CS_2$ type of functional group structure, with the exception of the dithiocarbamate compounds which contain a metal associated with the sulfur.

In this study, a model formulation (composition D) was used as a base composition. To this base composition was added 0.3 wt% of tetramethylthiuram monosulfide, tetraethylthiuram disulfide and copper dimethyldithiocarbamate to form compositions A, B and C, respectively. The cure profile of these model anaerobic compositions are shown in Figure 7, which demonstrates clearly that the metal ion, not the dithiolate functional group, is responsible for catalytc cure acceleration. Although the tetraethylthiuram disulfide and tetramethylthiuram monosulfide complexes have been known as very effective accelerators and vulcanizing agents in the synthetic rubber industries, these two compounds are found to be ineffective as accelerators for anaerobic cure systems.

## DISCUSSION

### The Role of Transition Metal

The adhesives studied here are active systems which cure by redox-initiated, free-radical polymerization using hydroperoxide as an initiator. However, the presence of catalytic amounts of metal ions in the system are essential in order to obtain an accelerated cure speed. The metal catalysis of peroxide decomposition for radical formation is well recognized.[26-27] The metal ions are oxidized while the hydroperoxide is reduced to form radicals which initiate polymerization of the monomer. The presence of both oxidizing and reducing agents in the system appears to be necessary for making a redox cycle. The role of transition metal in the redox radical production of the CHP/BS/amine system has been discussed by Boeder[28,29] and Okamoto.[30] The cure reactions are believed to have the following pathways: (1) the reaction of hydroperoxide with lower oxidation state metals results in the forma-

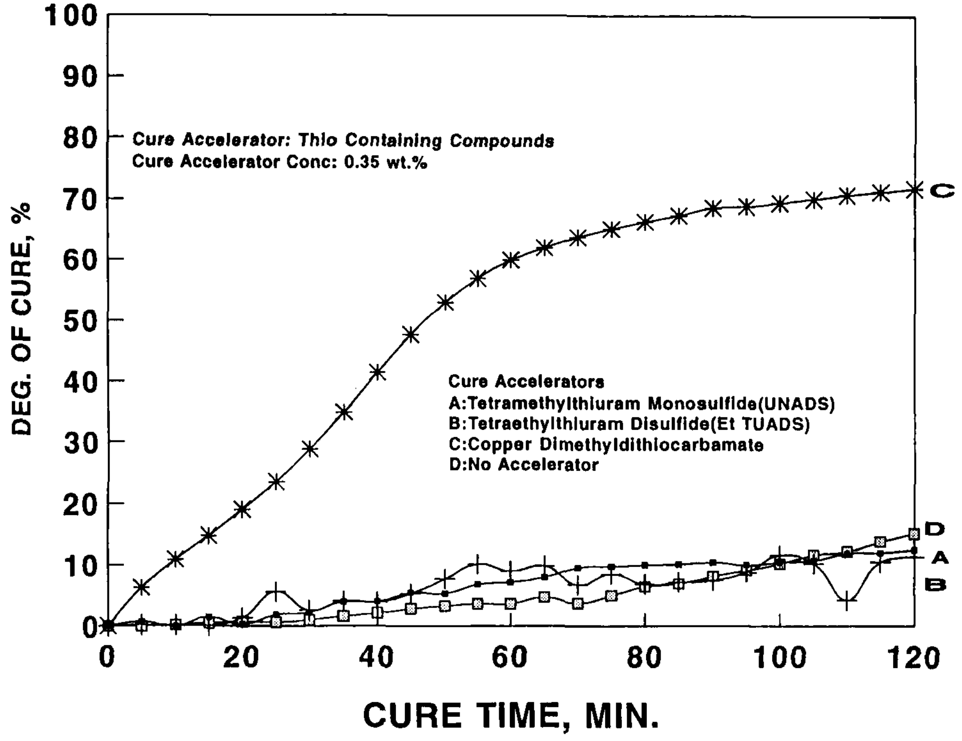


FIGURE 7 Plot of percentage cure *vs.* time of reaction for model anaerobic adhesive on the aluminum surface with the following thio-containing accelerators/catalysts: A: tetramethylthiuram monosulfide; B: tetraethylthiuram disulfide; C: copper dimethyldithiocarbamate; D: no catalyst.

tion of an active radical that can initiate polymerization; (2) the saccharin/amine complex reacts with metals in their higher oxidation states to reduce the metal oxidation state and to produce active radicals.

As pointed out by Rooney and Malofsky,[31] transition metals undergo a one-electron transfer reaction with hydroperoxides to generate free radicals as shown in the following reaction.

$$M^{n+} + RCOOH \longrightarrow M^{n+1} + RO^{\cdot} + OH^{-}$$

If no transition metal salts are added to the formulation, the metal ions formed at the adhesive/metal substrate interface region are believed to be the source of the metal for the catalytic decomposition of the hydroperoxide to form radicals which initiate polymerization of the monomer. The interaction of the oxidized metal ion with a reducing agent, such as l-acetyl-2-phenyl hydrazine (APH) or other amine compound, may be responsible for the reduction of the metal ions to their original valence state. Thus, the redox cycle of the metal ion causes the catalytic decomposition of hydroperoxide to be repeated. If the adhesive is to be used on a non-metallic surface, the addition of an active metal salt is necessary for an accelerated cure speed. As shown in the present study, the addition of catalytic amounts of a metal complex caused the cure activity to be enhanced, and the cure activity is more dependent on metal types than on ligand types of the metal complexes. Our data have shown that the catalytic activity of the metal is in the order of Cu>Ni≫Zn which appears to be related to the redox potential for these metals in various oxidation states. The reduction potentials for $Cu^{2+}/Cu^{+}$, $Ni^{2+}/Ni^{o}$, and $Zn^{2+}/Zn^{o}$ are 0.153, −0.257 and −0.7618 volts, respectively.[32]

### The Role of Saccharin

One of the most successful accelerator combinations has been saccharin, and an organic tertiary amine such as N,N-dimethyl-p-toludiene (DMPT).[11] Both saccharin and DMPT are accelerators by themselves. However, in combination they provide a synergistic effect in cure acceleration. The mechanism of this effect is still not clear. One likely explanation[33] for this phenomenon is that the amine functions as a mild reducing agent and converts the higher oxidation state metal ion to a lower oxidation state and saccharin acts as a solubilizing agent for metal from the surface of the substrate. It is also suggested[34] that the saccharin chelates the higher oxidation state metal ions and lowers the redox potential for reduction of that ion by the amine.

Boerio, *et al.*[35] have investigated the role which saccharin plays in the interfacial chemistry of an anaerobic adhesive comprising TRIEGMA/CHP/Acetylphenylhydrazine (APH)/BS on a silver surface using a Surface Enhanced Raman Scattering (SERS) technique. The results indicated that saccharin was preferentially adsorbed at the silver metal surface to form metal salts, which may play an important role in catalytic decomposition of the hydroperoxide for polymerization initiation of the adhesive. When saccharin was replaced in the curing system by benzoic acid, the SERS spectra also detected the formation of metal salt in the interfacial region. The acidic nature of both saccharin and benzoic acid appears to be responsible for this metal salt formation at the interface region. This observation seems to support the above explanation for the role of saccharin in anaerobic cure reactions.

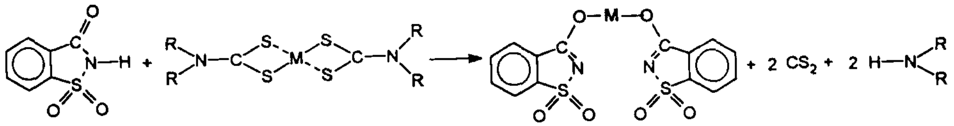
It must be pointed out that, in the present anaerobic system, neither the metal dithiolate catalyst nor the saccharin alone shows a significant acceleration effect; however, the combination of saccharin and metal dithiocarbamate gave a synergistic effect on cure acceleration. Although the mechanism is not yet clear, it is evident that saccharin plays an important role in the present anaerobic cure system.

The N—H group in saccharin is known to have a moderate acid strength. The $PK_a$ of saccharin is about 2.32. The pH of an 0.35 wt% solution of purified saccharin in water is about 2.036. Therefore, with such a high acid strength, one would expect that a metal saccharinate salt could be formed upon contact of saccharin with copper, nickel or zinc complexes. Evidence of the formation of copper, iron and zinc saccharinate upon a short contact (a few seconds) of these metals with a 0.1 wt% of aqueous saccharin solution was detected by a grazing angle FT-IR technique.[37]

Since no amine co-accelerator is present in our adhesives and the amount of the saccharin in the system is in excess of the metal dithiolate complexes (0.85 *vs.* 0.35 wt%), saccharin may function as an agent for interactive decomposition of dithiolate complexes which enhances the release of the active metal ions for catalytic decomposition of the hydroperoxide. It has long been known that dithiocarbamates are decomposed in an acid solution. The breakdown of dithiocarbamic acids into amines and $CS_2$ in the presence of acid has been used as the basis for the quantitative estimation of dithiocarbamates.[38] Zahradnik and Zuman[39,40] explained the acid decomposition of dithiocarbamate by a proton addition according to the following reaction.

$$R_2NCS_2^- + H^+ \longrightarrow R_2N\text{-}H + CS_2$$

The following reaction of the saccharin and metal dithiocarbamate is postulated to generate an ionic metal salt and an amine byproduct.



Where M = Cu, Ni and Zn

Therefore, the breakdown of the dithiocarbamate[41] may provide the amine which can function as a mild reducing agent for metal ion reduction. The saccharin may also function as a chelating agent for the oxidized metal ions and lower the redox potential for reduction of that metal ion. Thus, our data clearly demonstrate that this RT/FT-IR technique can be employed easily for evaluation of metal catalysis in anaerobic cure systems.

## CONCLUSIONS

RT/FT-IR has been used to monitor the cure kinetics of anaerobic adhesive formulations. The catalytic effect of several transition metal dithiolate complexes for redox-initiated polymerization of acrylates has been studied. The model formulation used in these studies contained triethyleneglycol dimethacrylate monomer, cumene hydroperoxide and saccharin. Additional compositions were prepared and tested by addition of various transition metal dithiolate catalysts which include the dithiocarbamate, dithioxanthate and dithiophosphate complexes of copper, nickel and zinc to the model formulation. Copper diacetylacetonate was also studied for comparison of its catalytic reactivity. The effects of catalyst concentration, ligand and metal types and co-initiator on cure profiles has been monitored in a real-time mode. The copper complexes were found to be the most effective catalyst for all systems studied. The catalytic activities of copper complexes were also found to be affected by the type of ligand, such as dithiocarbamate *vs.* xanthate and diacetylacetonate, associated with the copper metal. The zinc dithiolate complexes were found to be ineffective catalysts for anaerobic cure systems. A synergistic effect of saccharin and the copper complex for the presently studied anaerobic cure systems was also observed. In conclusion, with this RT/FT-IR technique, the effectiveness of various metal catalysts in anaerobic compositions can be easily evaluated as a function of time in a real-time mode. The utilization of this technique can also be extended to the evaluation of other reaction parameters such as types of resin, initiator, accelerator, inhibitor (or stabilizer) and reaction temperature, which are known to affect the anaerobic cure performance.

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41. It is speculated that one of the reaction products of copper dimethyldithiocarbamate (Cu-DMDTC)/BS/CHP system is dimethylamine (Fp 15°C) which is a gas in room temperature. However, the analyses of liquid and gaseous phase reaction products showed no detectable amount of dimethylamine using GC/MS/IR techniques in a closed vial. The reason could be due to the amine being oxidized by the peroxide or reacted with the acidic saccharin immediately upon its formation. A discoloration and exothermic reaction is detected upon the addition of the CHP to a toluene solution of BS/Cu-DMDTC indicating that a decomposition reaction has occurred.