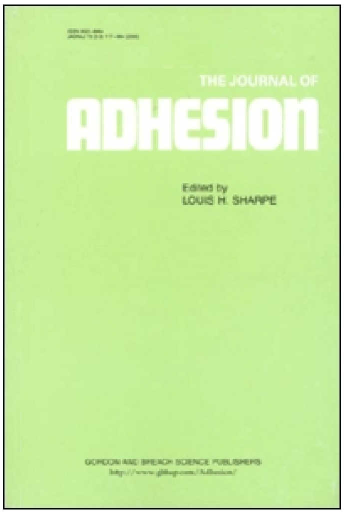

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Randall G. Schmidt[a]; James P. Bell[a]; Andrew Garton[a]
[a] Polymer Science Program, Institute of Materials Science, Box U-136, University of Connecticut, Storrs, CT, U.S.A.

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NOTE

Chemical Interactions Between Mercaptoester Coupling Agents and Steel

RANDALL G. SCHMIDT, JAMES P. BELL and ANDREW GARTON

Polymer Science Program, Institute of Materials Science, Box U-136, University of Connecticut, Storrs, CT 06268, U.S.A.

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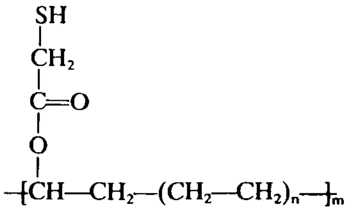
KEY WORDS Coupling agents; mercaptoester; adhesive durability; adhesive bonding; mechanism of bonding; interface characterization.

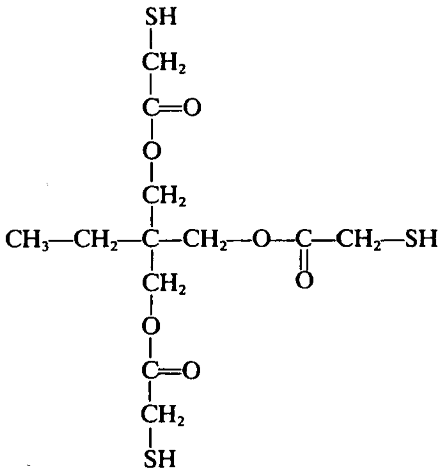
Poly(ethylenemercaptoester) coupling agents (EME, structure I) have been shown previously[1] to enhance both the initial peel strength and corrosion resistance of steel-epoxy adhesive joints. Their success was attributed to the ability of the mercaptoester functionality to interact chemically with both the epoxy resin and the steel surface, thus forming chemical bonds across the interface.



$$-\!\!\left[\begin{array}[b]{c} SH\\ | \\ CH_2\\ | \\ C{=}O\\ | \\ O\\ | \\ CH\end{array}\!\!-CH_2-(CH_2-CH_2)_n-\right]_m$$

EME, structure I

The reaction of EME with the epoxy resin can be demonstrated using infrared (IR) spectroscopy by following the decrease in epoxy (916 cm^{-1}) and thiol (2569 cm^{-1}) functionality, and the increase in hydroxyl (ca 3400 cm^{-1}) functionality.[1a] The purpose of this communication is to demonstrate the nature of the chemical interactions between EME and steel. In some cases, a model compound 1,1,1-trimethylolpropane trithioglycolate (TTTG, structure II, Evans Chemetics Co.) was used to better illustrate the chemical interactions.



TTTG, structure II

EXPERIMENTS AND RESULTS

EME coupling agents were synthesized as described previously.[1,2] TTTG was used as received. All solvents were reagent grade or better. Ultra-violet (UV) spectra were obtained in 1 cm quartz cells using a Perkin–Elmer 3400 spectrometer. Infrared (IR) spectra were obtained at 4 cm^{-1} resolution using a Nicolet SX-60 FTIR. Treated ferric oxide specimens were prepared for IR spectroscopic analysis by dispersion in potassium bromide discs. The IR spectra of the starting reagents and the precipitates from ferric chloride solutions were obtained as thin films on IR transparent supports.

(a) Interaction of EME and TTTG with ferric ions in solution

TTTG and EME were reacted with anhydrous ferric chloride solution (in methanol for TTTG and in octanol for EME) so as to examine their interactions in an environment simpler than the polymeric solid state. The addition of mercaptoester yielded a red precipitate which settled on the bottom of the container. A simple flame ionization experiment confirmed that the precipitate was an iron-containing complex. Figure 1 shows the UV spectra of the remaining solution, after addition of EME to ferric chloride solution in octanol. The continuous reduction of the ferric chloride absorption can be used to quantify the removal of ferric ions from solution. Ferric chloride solutions in methanol and octanol were shown separately to obey Beer's law; therefore Figure 2 indicates that TTTG removed ferric ions from methanol solution almost on a 3:1 molar basis, which is the same as one mole of ferric ion to one equivalent of thiol functionality (structure II).

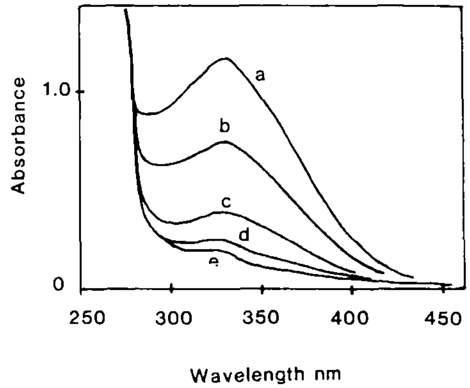


FIGURE 1 UV/vis spectra of ferric chloride solution after addition of EME. (a) 0.4 mg $FeCl_3$/10 cm^3 octanol (2.5×10^{-6} mol Fe), (b) $+4.6 \times 10^{-7}$ equivalents mercaptoester, (c) $+9.2 \times 10^{-7}$ equivalents mercaptoester, (d) $+1.4 \times 10^{-6}$ equivalents mercaptoester, (e) $+2.3 \times 10^{-6}$ equivalents mercaptoester.

The precipitates formed upon TTTG addition were examined by IR spectroscopy (Nicolet SX-60 FT-IR, 4 cm^{-1} resolution) after they were allowed to settle on a calcium fluoride disc, then rinsed with methanol and dried under nitrogen. The spectra in Figure 3 show TTTG and the TTTG-Fe precipitate. The spectra were normalized to a constant intensity of the C–H stretching absorptions at *ca.* 3000 cm^{-1}, so as to allow for different sample thicknesses. The most obvious difference between the two spectra is that the S–H absorption of TTTG at 2569 cm^{-1} was almost completely eliminated by reaction with ferric chloride. The

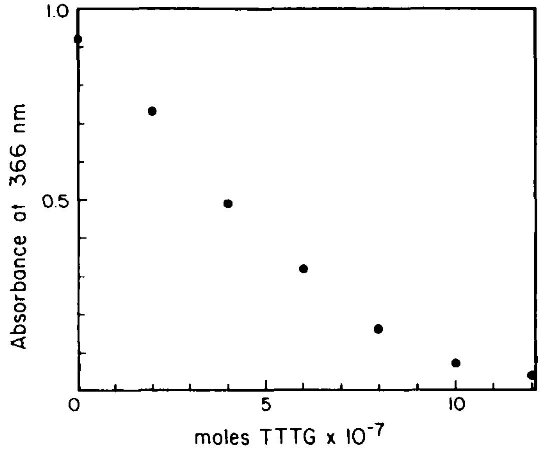


FIGURE 2 Absorbance of ferric chloride solution at 366 nm after addition of various amounts of TTTG. Initial $FeCl_3$ content of solution was 4.4×10^{-6} moles.

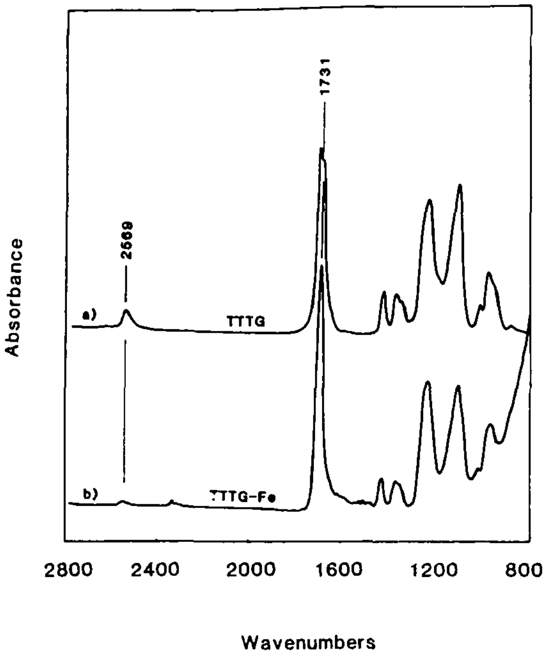


FIGURE 3 IR Spectra of (a) TTTG and (b) TTTG–$FeCl_3$ precipitate.

carbonyl absorption at *ca.* 1730 cm^{-1}, although not completely unchanged (see next section) did not exhibit the >50 cm^{-1} shift which would be characteristic of the formation of a coordination bond between the carbonyl group and the iron.[3] Note that the small absorption at *ca.* 2350 cm^{-1} is due to atmospheric carbon dioxide and should be ignored.

Spectra of the equivalent EME–$FeCl_3$ precipitate are shown in Figure 4; they

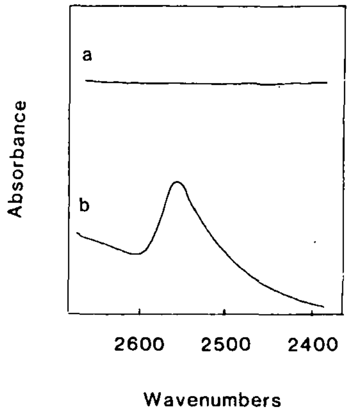


FIGURE 4 IR Spectra (thiol region) of (a) EME-$FeCl_3$ precipitate (b) EME.

demonstrate that the S–H functionality of EME was completely consumed in forming a precipitate with $FeCl_3$.

Since the ferric ion and thiol consumptions were approximately equivalent, a direct reaction between the two is implied, rather than catalytic effects of ferric ions on, for example, thiol loss by disulfide formation.

(b) Interaction of TTTG and EME with solid ferric oxide

A steel surface will always have an oxide overlayer. The interactions of the mercaptoesters with this oxide were examined by coating a high surface area ferric oxide powder with the coupling agent in a manner identical to that used to treat steel.[1] Figure 5 shows the IR spectra of TTTG and TTTG-coated ferric oxide again scaled to a constant C–H stretching intensity. As in Figure 3, the thiol absorption of TTTG was removed on reaction with the iron, and the carbonyl absorption experienced only a relatively small shift. Figure 6 shows that the EME coupling agent behaved in a similar manner to the TTTG model system. The thiol characteristic absorption was completely eliminated when the EME was coated onto ferric oxide. The spectra again were scaled to a constant C–H stretching absorption.

Figure 7 illustrates the changes in the carbonyl absorption of TTTG when coated on the ferric oxide. The carbonyl region of the EME-coated ferric oxide showed qualitatively similar effects. The apparent sharpening of the carbonyl stretch in the oxide coatings was at first sight puzzling, since one would expect a broadening and a decrease in frequency if the carbonyl group interacted with the

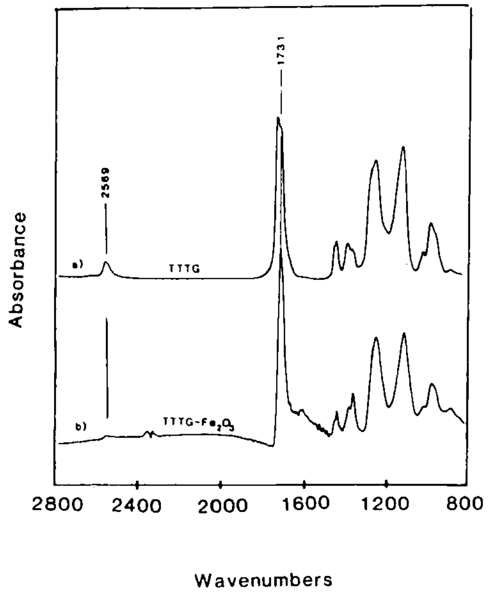


FIGURE 5 IR Spectra of (a) TTTG and (b) TTTG coated ferric oxide.

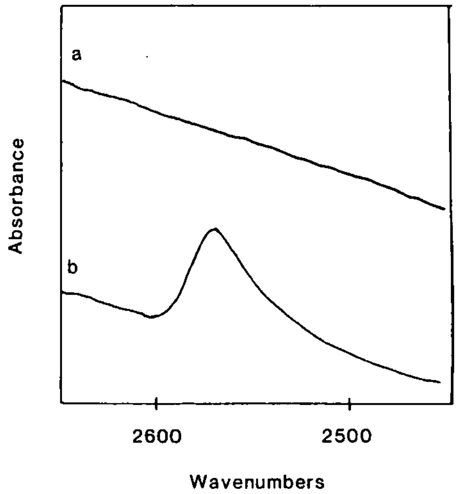


FIGURE 6 IR spectra (thiol region) of (a) EME coated ferric oxide (b) EME.

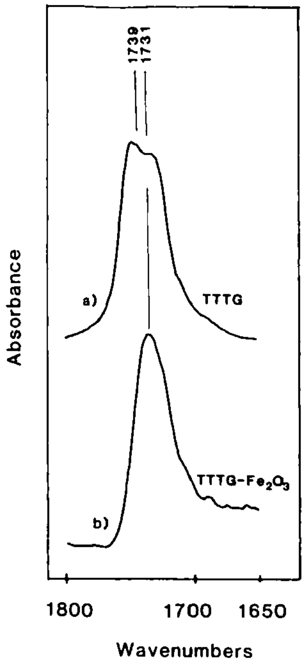


FIGURE 7 IR spectra (carbonyl region) of (a) TTTG and (b) TTTG coated ferric oxide.

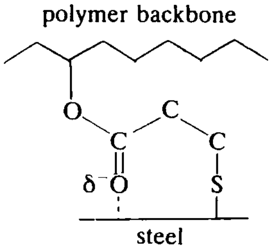
iron. However, it should be recalled that in the unreacted state the carbonyl groups of TTTG and EME will be at least partially hydrogen bonded to thiol groups. Reaction of TTTG and EME with the iron removes this opportunity for hydrogen bonding. The spectra in Figure 7 are therefore consistent with the following scenario: In the unreacted state, the carbonyl stretch absorption of TTTG and EME is comprised of a hydrogen bonded component at *ca.* 1725 cm^{-1} (broad), and a non-hydrogen-bonded state at 1739 cm^{-1}. Upon reacting with ferric oxide, the opportunity for hydrogen bonding is removed, but weak dipolar interactions with the iron move the carbonyl stretch frequency from 1739 cm^{-1} to 1731 cm^{-1}. Such a mechanism is consistent with observations on other ferric ion/thiol complexes, e.g. the ferric ion/EDTA/thiophenol complexes reported by Koch and Ackerman.[4]

CONCLUSIONS REGARDING CHEMICAL INTERACTIONS

The thiol functionality of TTTG and EME appear to react directly with the Fe^{3+} presumably with the elimination of a proton.

$$\mathrm{R-SH + Fe^{3+} \rightarrow R-SFe^{2+} + H^{+}}$$

The carbonyl functionality does not form a discrete coordination bond with the iron (i.e., to form a chelate structure) but is associated with the iron through relatively weak dipolar interactions. This is illustrated pictorially below, although some details of exact nature of the bonding require further verification.



However, although the carbonyl functionality is only weakly associated with the iron, it plays a significant role in the interaction, because model thiol compounds without ester functionality (e.g. 1 pentane thiol and 1,5 pentane dithiol) were appreciably less effective in scavenging ferric ions from solution in experiments analogous to Figures 1 and 2. This may be due to the lack of a polar interaction as described above, or inductive effects which change the acidity of the thiol.

Acknowledgements

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References

1. a. R. G. Schmidt and J. P. Bell, in *Adhesives and Sealants for Space and Harsh Environments*, (L. H. Lee, ed.), ACS Symp. Series, Plenum Press, New York, in press.
   b. R. G. Schmidt, Ph.D. Thesis, University of Connecticut, 1987.
   c. R. G. Schmidt and J. P. Bell, Proceedings of the ACS Division of Polymeric Materials: Science and Engineering **56,** 313 (1987).
2. R. G. Schmidt and J. P. Bell, *J. Adhesion,* in press.
3. F. P. Dwyer and D. P. Moeller, *Chelating Agents and Metal Chelates*, p. 124, Academic Press, New York (1964).
4. S. Koch and G. Ackerman, *Z. Anorg. Allg. Chem.*, **S20,** 203 (1985).