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ESEEM of Copper Complexes Formed in the Interlayer between Thiokol-Epoxy Adhesive and Brass Substrate

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Abstract. Copper complexes formed in the interlayer between the thiokol-epoxy adhesive and a brass substrate were studied by electron spin echo envelope modulation. The goal of the study was to help gain better understanding of the nature of the adhesion mechanism of polymer macromolecules with the brass substrate. Previous investigations revealed that square-planar copper complexes with sulphur-containing ligands form in the interlayer. However, a detailed structure of the copper-sulphur complex was not known. To get structural information we used a method that can be applied for weakly coupled nuclei with axially symmetric hyperfine interactions. The number of protons near the copper complex was estimated. Observation of nitrogen nuclei in the copper complex structure of the copper complex formed in the interlayer between the thiokol-epoxy adhesive and the brass sub-strate was proposed.

1 Introduction

Knowledge about the nature of the bond between polymer and substrate is of primary importance for optimizing the characteristics of adhesives. The study of the mechanism of adhesion of a thiokol-epoxy adhesive to a brass substrate was the subject of several investigations [1–3]. Electron paramagnetic resonance (EPR) studies of the interlayer between the adhesive and the brass substrate revealed the formation of square-planar copper complexes with sulphur-containing ligands. This conclusion was made by simulating the experimental EPR spectra and by comparison with the data on similar systems. It was found that the number of complexes depends on the free-sulphur concentration [1]. The diffusion of the copper ions from the substrate into the thiokol-epoxy polymer was studied with EPR imaging [2]. A correlation was found between the content of the free sulphur in the thiokol-epoxy adhesive and the adhesion strength to the substrate. However, a detailed structure of the copper-sulphur complex

was not known. In this work we used the electron spin echo envelope modulation (ESEEM) to probe the ligand arrangement of the copper complexes. This method proved to be very useful for obtaining structural information in ordered and disordered materials [4-6].

2 Experimental Procedure

The samples were prepared as described in ref. 1. They consist of 100 mass parts (m.p.) of thiokol polymer, 20 m.p. of epoxy polymer and 1.5 m.p. of a mixture of dimethylaminomethylphenol with 2,6-bis-dimethylaminomethylphenol. For our study we used mainly the sample with the maximum EPR signal (free-sulphur content, 20 m.p.). Several experiments were performed on the sample without free sulphur. Only the thin layer of adhesive with a thickness of less than 0.5 mm, contiguous with the brass was used. ESEEM and relaxation measurements were made at liquid helium temperatures on a homebuilt pulse X-band spectrometer in Kazan and at 18 K on a Bruker X-band pulse ESP 380 spectrometer at the ETH in Zurich. We used two-, three-, and four-pulse ESEEM, HYSCORE, and pulse electron nuclear double resonance (ENDOR) techniques.

3 Results and Discussion

Figure 1 shows the echo-detected EPR spectrum of the adhesive with sulphur. The two-pulse echo sequence 8 ns $-\tau$ -16 ns was used with a time delay of $\tau = 200$ ns between microwave pulses at the microwave frequency 9.714 GHz.



Fig. 1. Field-swept two-pulse ESE spectrum of the copper complex in the thiokol polymer adhesive with free sulphur. Numbers 1-3 denote the field positions where ESEEM measurements were made.



Fig. 2. Field-swept two-pulse ESE spectrum of the thiokol polymer adhesive without free sulphur.

The magnetic field was swept from 293.0 to 393.0 mT with steps of 0.1 mT. The echo-detected EPR spectrum of the sulphur-free sample is shown in Fig. 2.

The spectrum of the copper complex is considerably less intensive and is superimposed by a strong and narrow line at g = 2.018 (designated by R in Fig. 2). We suppose that this peak is due to broken bonds of the epoxy polymer. At 18 K this line saturates much easier than the spectrum of the copper complex; this strongly testifies the different nature of the two overlapping spectra. After adding free sulphur we could observe only the spectrum of the copper complex indicating the formation of chemical bonds. In addition, in the sulphur-free sample



Fig. 3. Two-pulse ESEEM magnitude spectrum of the copper complex in thiokol epoxy polymer adhesive.

the EPR spectrum of the copper complex is considerably less resolved than the spectrum of the sample with sulphur. We suppose that this is an indication for more structural disorder in the area surrounding the copper in the sulphur-free sample.

For the sample with sulphur, ESEEM measurements were made at the different positions of the EPR spectrum, in particular at the maximum EPR absorption (position 2 in Fig. 1) and at the single crystallike positions g_{\parallel} (positions 1 and 3). Figure 3 shows the two-pulse ESEEM spectrum obtained at position 2. It is distinguished by peaks at the proton nuclear Zeeman frequency of about 15 MHz and at twice this frequency close to 30 MHz. Several lines in the lowfrequency region can tentatively be assigned to nitrogen that is expected to be in the sample. All these lines present at other two-pulse ESEEM spectra are obtained in different points of the echo-detected EPR spectra. Small peaks around the proton line were not analyzed because they were within the experimental error.

We could not find resolved spectra due to hyperfine interactions of electron spins with near protons by pulse EPR methods that are known for their high spectral resolution, like four-pulse ESEEM, HYSCORE and pulse ENDOR, so the value of the interactions is small.

To get additional structural information we used a method which can be applied for weakly coupled nuclei with axially symmetric hyperfine interactions [6, 7]. Here we give some basic relations that are necessary for experimentalists to follow the treatment of our experimental results.

The expression for the two-pulse ESEEM time-domain signal for one electron spin and one 1/2 nuclear spin with averaging in all orientation for a disordered system is given by [6]

$$\langle V(\tau) \rangle = 1 - \frac{3}{10} \frac{T_{\perp}^{2}}{v_{i}^{2}} [2 - 4F(T_{\perp}\tau)\cos(2\pi v_{i}\tau) + \cos(4\pi v_{i}\tau) + F(2T_{\perp}\tau)], \qquad (1)$$

where T_{\perp} is the perpendicular component of the anisotropic hyperfine tensor, v_i is the nuclear Zeeman frequency, and τ is the time delay between the two microwave pulses. Equation (1) is valid in the extremely weak hyperfine interaction limit, when $v \gg T_{\perp}$ and the isotropic hyperfine interaction parameter is supposed to be zero [6]. The function

$$F(T_{\perp}t) = \frac{15}{4} \int_{0}^{\pi} \{\cos^2\theta \sin^2\theta \cos[\pi T_{\perp}t(1-3\cos^2\theta)]\sin\theta\} d\theta , \qquad (2)$$

with $t = \tau$ or 2τ , describes the damping due to the hyperfine interaction. It can be seen from Eq. (1) that only the Zeeman frequency gives a contribution to the damped oscillations. For a quantitative description of the proton modulations in the two-pulse ESEEM the parameter

$$\lambda(\tau) = 1 - V_{\min}(\tau) / V_{\max}(\tau) , \qquad (3)$$

was used, where $V_{\min}(\tau)$ and $V_{\max}(\tau)$ are the minimum and maximum envelope amplitudes of $V(\tau)$, respectively.

This parameter is in fact the modulation amplitude and can be easily estimated from the experimental results. It was found [7] that for small τT_{\perp} values one can expand $\lambda(\tau)$ in a series and obtain that $\lambda(\tau)$ is linearly dependent on τ^2 . If the electron spin interacts with N nuclei, the observed modulation amplitude $V^{(N)}(\tau)$ is the product of the modulation amplitude $V_i(\tau)$ of each electronnuclear pair (a so-called "product rule") [6].

For disordered systems and neglecting spatial correlations of the magnetic nuclei one can write:

$$\langle V^{(N)}(\tau) \rangle = \prod_{i=1}^{N} \langle V_i(\tau) \rangle.$$
 (4)

According to Eq. (4) for spin systems with more than one nucleus, combination frequencies (more than one) will appear in ESEEM. With this relation we find for the experimental parameter $\lambda(r)$:

$$1 - \lambda^{(N)} = \prod_{i=1}^{N} (1 - \lambda_i^{(1)}) , \qquad (5)$$

where $\lambda^{(N)}$ and $\lambda^{(1)}$ designate modulation amplitudes due to N and 1 nuclei respectively. From these relations one can get only integral values of the hyperfine interaction tensor. Therefore it is assumed that the nuclei are located in several spheres. Usually one or two spheres of local nuclei are considered in disordered systems. In the *j*-th sphere with a radius r_j there are N_j nuclei. In the case of several spheres one should expect linear regions in the experimental dependence of $\lambda(\tau)$ for small τ^2 . For two-pulse ESEEM it is important to subtract the contribution of the double Zeeman frequency from the modulation pattern. The remaining part of the contribution from the close nuclei can be treated to get $\lambda_j^{(N)}$ for each sphere and then to express them through $\lambda_j^{(1)}$. To calculate $\lambda^{(1)}$ we used a relation obtained from the series expansion of $\lambda(\tau^2)$ [7]:

$$\lambda^{(1)}(0) = \frac{2\lambda'}{2av_i^2 \delta\lambda(\ln\delta\lambda) + \lambda'},\tag{6}$$

where $\lambda' = d\lambda^{(N)}/d\tau^2 |_{\tau=0}$, $\delta\lambda = 1 - \lambda^{(N)}(0)$, and $a = 5\pi^2/42$.

We then find for the anisotropic hyperfine coupling:

$$T_{\perp} = \sqrt{\frac{5\nu^2}{12}\lambda^{(1)}(0)} , \qquad (7)$$

and for the number of nuclei:

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$$N = \frac{\ln[1 - \lambda^{(N)}(0)]}{\ln[1 - \lambda^{(1)}(0)]}.$$
(8)

For paramagnetic centers with the localized spin density interacting with rather remote nuclei it is reasonable to apply the point-dipole approximation to calculate the distance to each surrounding sphere:

$$T_{\perp} = \frac{\mu_0}{4\pi} \frac{g_e g_n \beta_e \beta_n}{r^3 h} , \qquad (9)$$

where μ_0 is the vacuum permeability, g_e and g_n are the electron and nuclear gfactors respectively, β_e is the Bohr magneton, β_n is the nuclear magneton, and h is the Planck constant.

We would like to point out that the formulae we used for the analysis were obtained under the assumption that the microwave pulses excite the whole EPR spectrum. In our experimental conditions we can excite only a part of the EPR spectrum. In our case the linewidth of the EPR spectrum is defined mainly by g-value anisotropy and not by the ligand hyperfine interaction anisotropy. The criterion of the application of the analytical formulae under partial excitation of the EPR spectrum in the weak hyperfine interaction limit was given in ref. 6 (chapter 9, fig. 5). Because the ratio of the amplitude of the microwave pulses v_1 and the proton Zeeman frequency v_1 are close to 4 in our experimental conditions, the amplitude of v_1 and $2v_1$ harmonics is close to the maximum (see ref. 6, fig. 5 in chap. 9). This means the strong v_1 limit and corresponding analytical formulae can be used in our analysis.



Fig. 4. Dependence of the experimental parameter $\lambda(\tau)$ on τ^2 . The parts 1-3 of the curve represent the contribution of the first and the second sphere and of the matrix protons to the modulation pattern, respectively.

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Figure 4 shows the dependence of $\lambda(\tau)$ on τ^2 , obtained from the experiment at position 3 of Fig. 1. The double Zeeman frequency was removed from the plot with fast Fourier transformation (FFT) of the time-domain pattern, subtracting the double Zeeman frequency peak and with backward FFT.

For the first proton sphere the application of Eqs. (6)–(9) to our experimental data yields $N \approx 2$, with a dipolar hyperfine coupling $T_{\perp} \approx 3$ MHz, and $r \approx 0.3$ nm, and for the second sphere it yields $N \approx 4$, with $T_{\perp} \approx 1.4$ MHz, and $r \approx 0.4$ nm.

As this method is rather approximate, we tried to fit the time-domain ESEEM data with the obtained parameters. For example, the time-domain ESEEM plot (measured at position 3 in Fig. 1) and best fit according to Eqs. (1) and (2) are given in Fig. 5. It should be noted that we did not take into account the modulation due to N nuclei. Hence one can see low-frequency oscillations on the time-domain plot. We could achieve best fit for a proton arrangement taking $N \approx 6$ with $T_{\perp} \approx 1.4$ MHz, and $r \approx 0.4$ nm. The time-domain ESEEM plots at positions 1 and 2 in Fig. 1 can be fitted with approximately the same set of the parameters, confirming the structure model of the copper-sulphur complexes we suggest below.

The low-frequency lines in two-pulse ESEEM FT spectra are probably due to ¹⁴N nuclei. From structural considerations they should be rather remote from the copper. Hence one expects a weak coupling case, i.e, the hyperfine coupling small compared with the nuclear Zeeman interaction. We suppose that the observed frequencies are close to the nuclear quadrupole resonance frequencies of ¹⁴N given by

$$\nu_{-} = 2K\eta, \qquad \nu_{0} = K(3 - \eta), \qquad \nu_{+} = K(3 + \eta), \qquad (10)$$

where $K = e^2 q Q/4h$ is the quadrupole coupling constant, and η is the asymmetry parameter.

Assigning the ¹⁴N lines as $v_0 = 0.980$ MHz, $v_- = 2.696$ MHz, $v_+ = 3.676$ MHz in Fig. 3, we obtained $K \approx 1.06$ MHz, and $\eta \approx 0.461$ for the nitrogen nuclei.



Fig. 5. Time-domain ESEEM plot (dashed line) and best fit (solid line) according to Eqs. (1) and (2). Low-frequency oscillations are due to N nuclei.



Fig. 6. Proposed structure of the square-planar copper-sulphur complex in the interlayer between thiokol epoxy polymer and the brass substrate. The copper ion (Cu) is encircled by four sulphur ions (S). The closest two protons are marked by 1, the next four protons are marked by 2.

On the basis of our experiments we propose the structure for the square-planar copper-sulphur complexes shown in Fig. 6. Two closest protons 1 form hydrogen bonds. They compose the first proton sphere. The number of protons in the next sphere can vary from four to eight depending on the number of thiokol polymer molecules. Our experimental results support that the copper complexes have four protons 2 in the second proton sphere. The detection of remote nitrogen nuclei 3 agrees well with the assumption [3] that dimethylaminomethylphenol acts as an initiator.

4 Conclusions

The structure of the copper complex formed in the interlayer between the thiokolepoxy adhesive and a brass substrate was presented. Observation of nitrogen nuclei in the copper complex structure agrees well with an earlier conjecture that dimethylaminomethylphenol acts as an initiator of the reaction of polymerization.

The interaction unit [3] of the polymer macromolecules with copper ions could be evaluated, giving an idea about the polymerization mechanism of thiokol epoxy polymers and about the heterogenic function of the copper sulphide in the polymerization process.

The application of ESEEM methods to study the interaction mechanism of the polymer macromolecules with the brass substrate is proved to be very useful for a better understanding of the nature of adhesion.

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References

- Nefed'ev E.S., Mirakova T.Yu., Averko-Antonovich L.A., Kadirov M.K., Il'yasov A.V.: J. Adhesion Sci. Technol. 5, 691–695 (1991)
- Nefed'ev E.S., Musin K.M., Mirakova T.Yu., Kadirov M.K., Aminov K.L., Salikhov K.M., Silaev V.A.: Appl. Magn. Reson. 11, 115-123 (1996)
- 3. Nefed'ev E.S., Silaev V.A., Mirakova T.Yu., Kadirov M.K., Il'yasov A.V.: Polymer 33, 3911-3915 (1992)
- 4. Schweiger A. in: Modern Pulsed and Continuous-Wave Electron Spin Resonance (Kevan L., Bowman M.K., eds.). New York: Wiley 1990.
- 5. Kevan L. in: Time Domain Electron Spin Resonance (Kevan L., Schwartz R.N., eds.). New York: Wiley 1979.
- 6. Dikanov S.A., Tsvetkov Yu.D.: Electron Spin Echo Envelope Modulation (ESEEM) Spectroscopy. Boca Raton: CRC Press 1992.
- 7. Astashkin A.V., Tsvetkov Yu.D.: Appl. Magn. Reson. 6, 411-426 (1994)

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