Structural Study of a Varnish by Electron Spin Resonance

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SYNOPSIS

Related to the study of interactions between food and aluminum cans, structural features of a vinylic organosol coating were studied by electron spin resonance (ESR). Paramagnetic probes were incorporated separately in the normal formulation of a widely used varnish, which was then cured at high temperature for different times. The behavior of aminoxyl probes, differing by their volatility and their functional groups, was studied. When 4-amino-2,2,6,6-tetramethylpiperidinoxy (**3**) was used as probe, it grafted onto the polymeric chains during curing. Two transitions could then be observed, corresponding to NO· in two environments, which were assigned to the PVC (T_{fs}, 132–142°C) and to the epoxyphenolic (EP) (T_{50G}, 142–152°C) phases of the varnish. This was confirmed by a separate study of the PVC and EP constituents. Both transition temperatures depended on the extent of curing, suggesting that the PVC phase was plasticized by reactive constituents of the coating. The transition temperatures were also influenced by the extent of penetration of the PVC in the EP phase. Probes which could not graft on the polymer were lost by volatilization during curing. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Aluminum food cans are often coated inside with varnishes which behave as a barrier between metal and food. The varnishes employed for food cans are mainly polyesters, epoxyphenolics, and vinylic organosols.[1,2] The polyesters, synthesized from polyols and polyfonctional acids, have a medium flexibility and chemical resistance. Epoxyphenolics associate two families of polymers (epoxy and phenolic) with complementary properties that enable preparation of varnishes with good chemical resistance. Vinylic organosols are vinylic polymers based on poly(vinyl chloride) (PVC) reinforced by phenolic resins or by other resins; they are very flexible in combination and chemically resistant. The PVC part leads to a good flexibility and facility of processing; the epoxyphenolic (EP) part ensures the adhesiveness to the metal by its polar groups and a barrier role due to its tridimensional structure.

Food-polymer interactions have been mainly demonstrated indirectly, by following the migration of residual monomers or of technological additives into food.[3–5] The penetration of food into packaging has been demonstrated by weight uptake,[4] by the use of radioactive tracers,[5] microscopic techniques,[6] or by electron spin resonance (ESR).[7–9] A modification of the structure of the polymeric network of PVC was observed by ESR after contact with water or fatty media; this was related to the penetration of food simulants into the polymeric network. We intend to study interactions between a varnish (vinylic organosol) and food by ESR, using paramagnetic probes. A prerequisite for such studies is the knowledge of the structure of the coating and the behavior of paramagnetic probes before contact. The first part of our work is described in this article.

EXPERIMENTAL

Paramagnetic Probes

Four probes having different polarities, volumes, and functional groups were chosen: 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) (**1**), 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl(4-hydroxy-TEMPO) (**2**), 4-amino-2,2,6,6-tetramethylpiperidin-1-oxyl(4-

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Journal of Applied Polymer Science, Vol. 62, 2219–2228 (1996)
 CCC 0021-8995/96/132219-10

amino-TEMPO) (**3**), and 4-dimethylamino-2,2,6,6-tetramethylpiperidin-1-oxyl (4-dimethylamino-TEMPO) (**4**) (Fig. 1). **1**, **2**, and **3** are commercial products available from Aldrich-Chemical; **4** has been synthesized in our laboratory.[10]

Preparation of Probe Containing Polymers

The constituents of the varnish and the varnish itself were kindly provided by Holden Europe. The vinylic organosol was provided in a form of viscous resin. Probes were added to the solution in quantities of 750 ppm (relative to dry weight) for probes **3** and **4**, and in quantities of 750 and 1500 ppm for probes **1** and **2**. To obtain a normally cured varnish (0), the mixture was applied on an aluminum foil or a tined-steel plate. On aluminum it was cured 24 s at 290°C (quick cure conditions for a normal food can). After cooling, it was placed in a mercuric chloride solution (8%) to separate the varnish film from the aluminum foil. On steel, it was cured 24 s at 315°C, then separated from the support using mercury: the varnish was incised, and a drop of mercury was poured on the incision; the mercury amalgamated the tin, which allowed an easy removal of the varnish; the film was then wiped and analyzed. Unless specified in the text these two curing methods were used for all experiments. The films of varnish (or membranes) obtained using aluminum foil or tined-steel plate were 12 ± 1 μm thick and the two cures corresponded to the same Peak Metal Temperature.

For under- and over-cured varnish (respectively −5 s and +5 s), the mixture was applied on aluminum only. It was cured 19 and 29 s at 290°C, respectively. It was then removed from the support as described above.

We also studied the behavior of the probe in each constituent of the coating: the epoxyphenolic (EP) and the PVC resins.

The EP resin was a mixture prepared specifically from the usual components of the varnish. To prepare a film of epoxyphenolic, the same procedure as above was employed.

PVC resin is the one entering in the composition of varnish. The probes were added to the powder and mixed in a mortar. The obtained blend was put into a plugged flask and placed in an oven 15 min at 80°C. This procedure was used to allow the diffusion of the probes in the material without degrading the PVC resin.

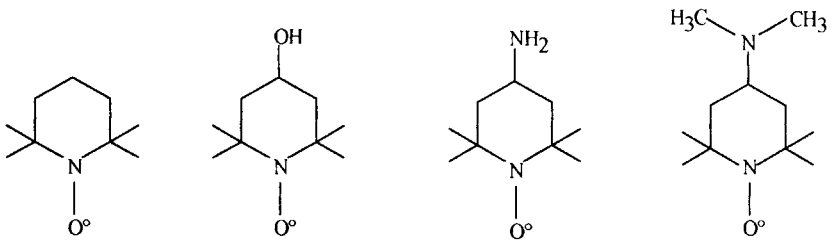
Spectrophotometer

ESR spectra were measured with a BRUKER ESP 300 spectrometer, operating at 9.6 GHz, with an ESP 1620 calculator. Spectra were measured in the temperature range of 300–450 K using a Brucker Variable Temperature Unit.

ESR Measurements

A varnish sample (2×4 cm^2) was rolled into a small cylinder, placed in a 30 cm ESR tube, and analyzed directly in the spectrometer cavity.

The hyperfine split (2 Azz, Fig. 2) of the spectrum was measured as the distance in Gauss between the two extreme peaks A–C (0.5 G resolution). The temperature at which the lines D and E were appearing was defined as T_{fs} (temperature fast signal). T_{50G}, the temperature characteristic of the mobility of the probe, has been defined experimentally[11] as the temperature which corresponds to 2 Azz = 50 G. The curve describing the evolution of 2 Azz against temperature changes curvature at 50 G = the radical passes from a slow motion to a rapid motion. Identical spectra were always obtained by applying the same temperature sequence a second time.



1 TEMPO 2 4-hydroxy-TEMPO 3 4-amino-TEMPO 4 4-dimethylamino-TEMPO

Figure 1 Chemical structures of the spin probes.

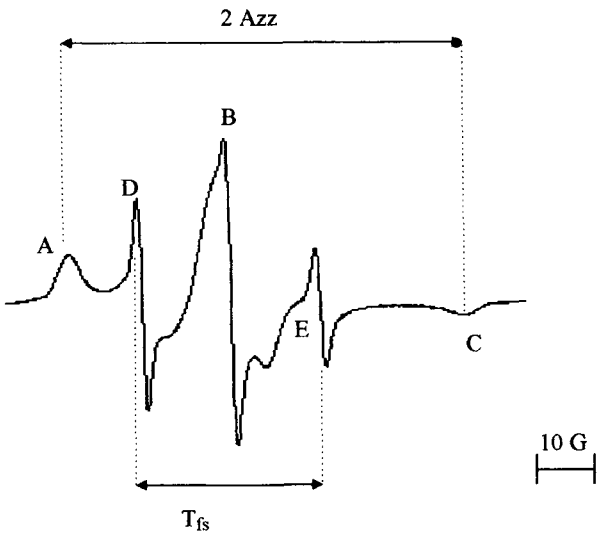


Figure 2 Measurements of ESR spectra.

Differential Scanning Calorimetry Measurements (DSC)

Differential scanning calorimetry (DSC) measurements were made using a METTLER TA3000 instrument (processor TC10) and a Print Swiss MATRIX recorder. All samples (9–12 mg) were initially heated from 30 to 150°C at a heating rate of 20°C/mn, followed by programmed cooling with liquid nitrogen. Glass transition temperatures (T_g) were measured by the midpoint method. Because there is an annealing peak in the first run using DSC, which would disturb the T_g value, we used the data of the second run as the experimental value of T_g.

RESULTS

Differential Scanning Calorimetry

To understand the influence of the nature of the metal supporting the varnish and the influence of the incorporation of probes in the material, we have measured the glass transition temperatures by DSC. The results are summarized in Table I.

Whatever the metal and the probe used, T_g is always equal to 76°C. It can be therefore assumed that the type of metal support and the probes in concentration from 750 to 1500 ppm do not influence this transition in the polymer. Even when the sample was heated up to 250°C, no second transition attributable to a second phase was observed.

Behavior of Probes in the Varnish: Analysis at Room Temperature

The ESR spectra at room temperature of the four probes incorporated separately in the varnish are shown in Figure 3.

The spectra of probes 1–4 differ in intensity and shape. TEMPO **1** and 4-hydroxy-TEMPO (**2**) give spectra with a single broad line of low intensity. These spectra are characteristic of aggregates.[12] 4-amino-TEMPO **3** and 4-dimethylamino-TEMPO **4** present wide and dissymetric spectra with three lines. These spectra are characteristic of dispersed and slow rotating probes.[7]

Probes **1**, **2**, and **4**, which probably evaporate during curing of the varnish, present weaker spectra than probe **3**.

Behavior of Probes in the Varnish: Analysis Above Room Temperature

The ESR spectra of TEMPO **1** and 4-amino-TEMPO **3** in the varnish, when the sample is heated from 30°C up to 180°C, are shown in Figure 4.

Whatever the temperature, the spectra of TEMPO remain those of an aggregate. For 4-amino-TEMPO [Fig. 4(b)], a gradual deformation of the spectrum is observed up to 110°C; at 120°C a shoulder is seen between lines A–B. At 145°C, two other lines (D and E) appear. As the temperature further increases, lines A and C are hidden by lines D and E growing in intensity. Above 145°C, the signal undergoes the characteristic changes into a sharp narrow triplet corresponding to NO$^{\bullet}$ which are well dispersed in the polymer and move quickly.[12] At 180°C, the maximum temperature allowed by the variable temperature unit, this spectrum was not reached. The plot of the hyperfine split (2 Azz) against tem-

Table I Influence of the Metal Used and of the Addition of Probes to the Varnish on Glass Transition Temperatures (T_g)

Probe	Quantity (ppm)	Steel Plate T_g (±1°C)	Aluminum Foil T_g (±1°C)
Without probe	0	76.5	76.4
TEMPO	750	75.9	
	1500	76.2	76.7
4-hydroxy-TEMPO	750	76.1	
	1500	76.9	76.3
amino-TEMPO	750	76.0	76.3

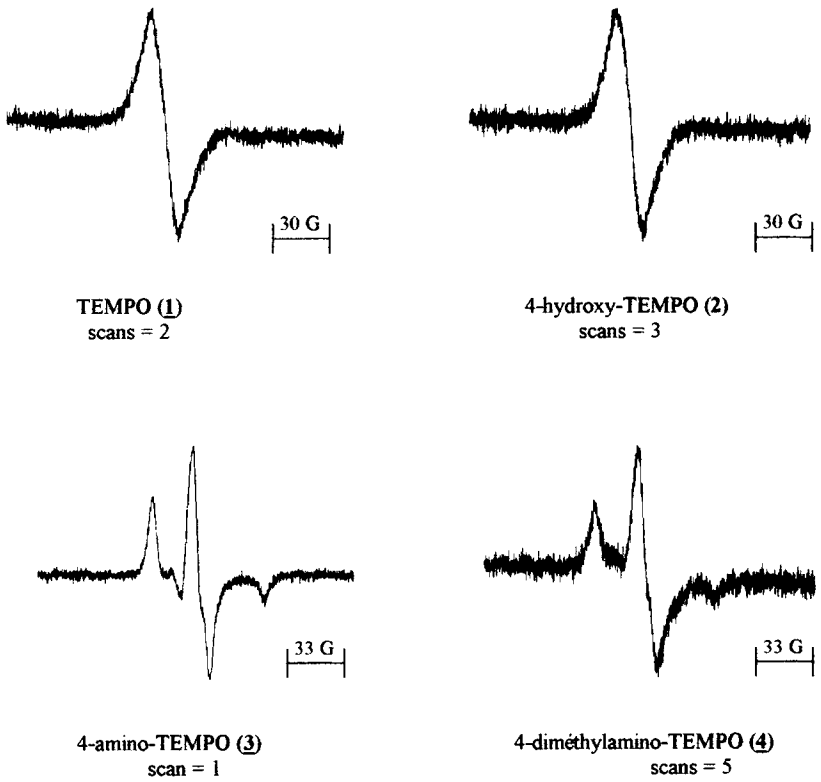


Figure 3 First-derivative ESR spectra of probes **1**, **2**, **3**, and **4** in the varnish, analysis at room temperature.

perature is shown in Figure 5 for the lines A, B and C and the lines D, B and E. 2 Azz takes the characteristic value of 50 G around 152°C. Lines D and E (second environment) can only be observed above 142°C. The spectrum recorded at 145°C was a composite spectrum, suggesting a study of the same probes in each component of the varnish separately: the PVC phase and the EP phase.

Behavior of the Probes in PVC and EP Phase: Analysis at Room Temperature

The ESR spectra of probes **1**, **2**, and **3** added separately to the PVC (a) and to the EP (b) components at room temperature are shown in Figure 6.

Whatever the material, 4-amino-TEMPO 3 displays the same behavior as in varnish (Fig. 3), with slow motion and a reduced orientational freedom. TEMPO **1** and 4-hydroxy-TEMPO **2** show spectra of aggregate in EP just as in the varnish (Fig. 3). In the PVC phase these probes are well dispersed and their spectra are characteristic of slow movement. The intensities of the spectrum in the varnish and in EP are much lower for probes **1** and **2** than for probe **3**.

Transitions in the PVC and the EP Constituents: Analysis Above Room Temperature

The aggregates' spectra of probes **1** and **2** do not change with increasing temperature from 20 to 180°C. We therefore focus on 4-amino-TEMPO.

The evolution of the spectrum of 4-amino-TEMPO with temperature is shown in Figure 7. In PVC (a) at 30°C, a spectrum consisting of three broad and dissymetric lines is observed. As the temperature is raised the signal distorts, and the width of the spectrum decreases from 2 Azz = 64 G at 30°C to 2 Azz = 35 G at 140°C. The signal thus changes to a sharp spectrum corresponding to fast motion. No composite signal indicating the presence of a second environment was observed. The graph describing the hyperfine split against temperature (Fig. 8) assumes the value of 50 G at 115°C.

In EP (b) little change in the spectra occurred when the sample was heated from 30 to 180°C; the fast signal was not reached. The spectrum at 180°C was still representative of slow motion, the width of the spectra still being above 50 G (Fig. 8). A second environment was never detected.

These experiments showed that the 4-amino-TEMPO is distributed in the two phases of the var-

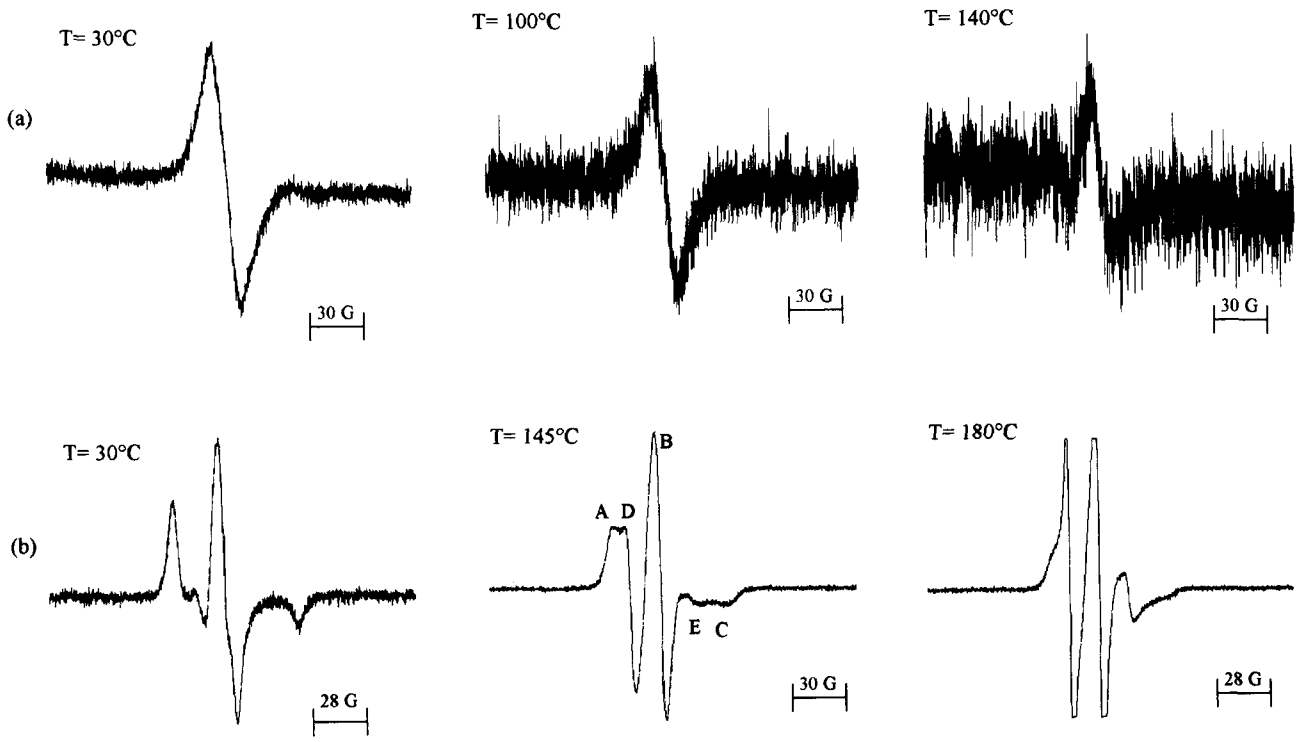


Figure 4 ESR spectra of TEMPO (a) and amino-TEMPO (b) in the varnish when the sample is heated from 30 to 180°C.

nish. The composite spectrum obtained corresponded to the existence of two environments in the varnish: one corresponding to PVC, the other to the epoxyphenolic phase. As transitions in polymers can be studied using paramagnetic probes, we studied the influence of the cure of the varnish with 4-amino-TEMPO **3** and 4-dimethylamino-TEMPO **4**. The latter compound was selected since it did not display spectra of aggregates.

Influence of the Cure of the Varnish on the Probes' Behavior: Analysis at Room Temperature

Figure 9 represents ESR spectra at room temperature of a varnish which was undercured (−5 s), normally cured (0), and overcured (+5 s).

The spectrum of the varnish which has been undercured and normally cured showed that the probe was immobilized. The spectrum of probe **4** was of lower intensity (evaporation of the probes during curing). When the varnish was overcured the two probes did not behave in the same way. Probe **4** exhibited a weak signal of an aggregate, similar to that obtained with probes **1** and **2**.

Since probe **3** does not result in aggregates, we studied the evolution of the coating with temperature for different curing using this probe.

Evolution Above Room Temperature of the Transitions for Different Curing of the Varnish Labeled with 3

At room temperature, the shapes of the spectra obtained with different degrees of cure were identical when the temperature was raised. The transitions observed occurred at different temperatures. The results are summarized in Table II.

With an overcured membrane it was not possible to determine T_{50G} and T_{fs} on account of the maximum temperature allowed by the instrument (180°C). This suggested that these transition temperatures were higher than 180°C. However, with under or normally cured membranes the two transitions (T_{50G} and T_{fs}) were clearly observed below 160°C.

DISCUSSION

The study of various probes in a varnish showed that their behavior depended on their volatility and on their functional groups. The spectrum of TEMPO **1**, 4-hydroxy-TEMPO **2**, and 4-dimethylamino-TEMPO **4** in the varnish at room temperature (Fig. 3) exhibited weak signals. This could be due to an

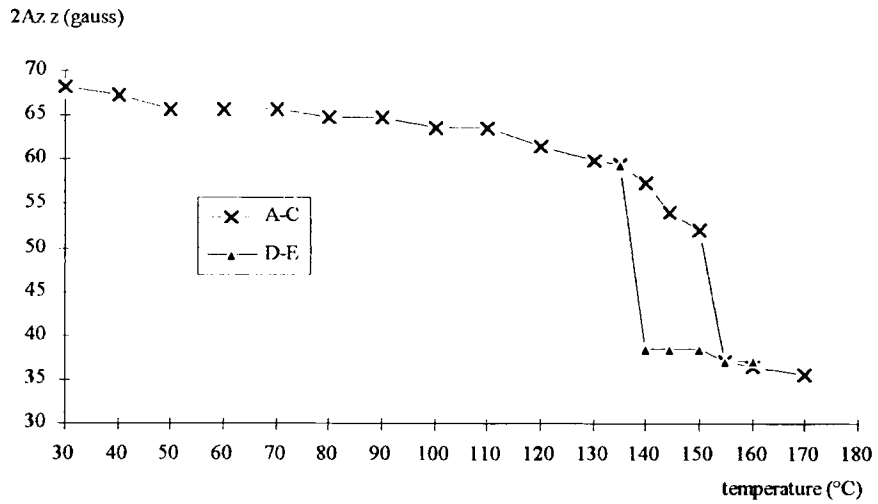


Figure 5 Evolution of hyperfine split (2 Azz) against temperature for the peaks A–C and D–E.

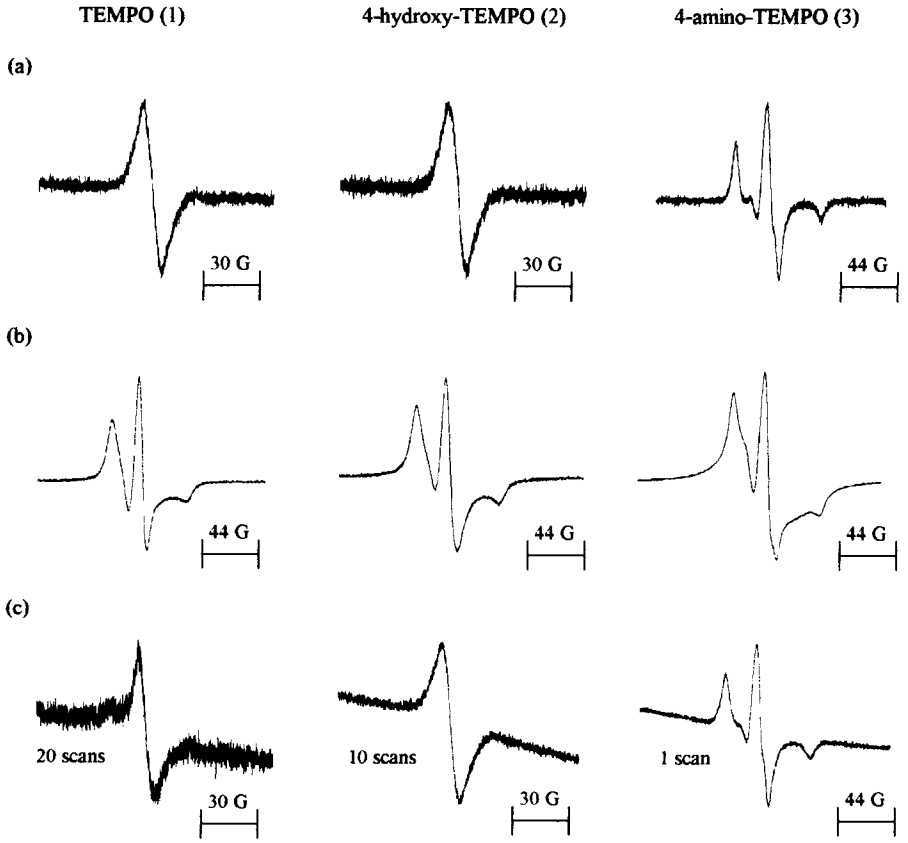


Figure 6 ESR spectra (at room temperature) of probes **1**, **2**, and **3** in the different materials: (a) varnish, (b) PVC, (c) EP.

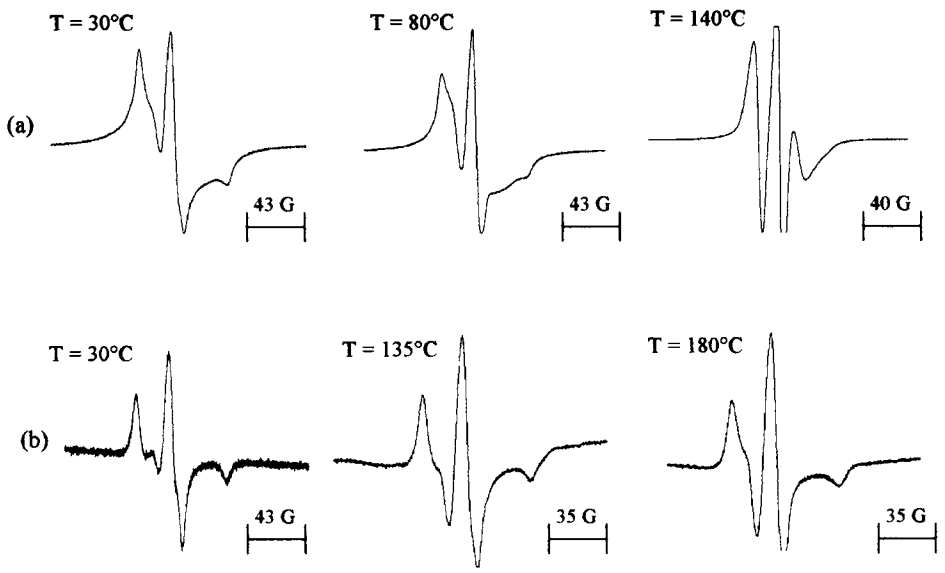


Figure 7 Evolution of the ESR spectra shape with the temperature at which the materials are heated: (a) PVC, (b) EP.

evaporation during the cure of the varnish or to reactions of NO°. It is well known that aminoxyls can react in presence of acids like HCl (arising from the degradation of PVC). This hypothesis can be rejected for three reasons: first, 4-amino-TEMPO **3**, which is also an aminoxyl, displayed a hundred times more intense spectrum (Fig. 3). Secondly, it has been shown that aminoxyls can be added to PVC materials processed at high temperatures without high decay.[7] Finally, a loss of intensity was also observed in the epoxyphenolic phase alone (Fig. 6). It could therefore be assumed that probes **1**, **2**, and **4** evaporated during curing of the varnish. This was certainly enhanced by the small thickness of the film (around 12 μm).

As described in the literature,[13] a signal of an immobilized probe has been observed for TEMPO in PVC. In varnish, the formation of aggregates observed with probes **1**, **2** (normal cure Fig. 3), and **4** (overcured Fig. 9) was surprising: aggregates indicate strong spin–spin interaction due to high local concentration of spins, while their average concentration in the varnish was low. It could be assumed that before evaporating, the probes were rejected into preferential zones near the surface of the varnish.

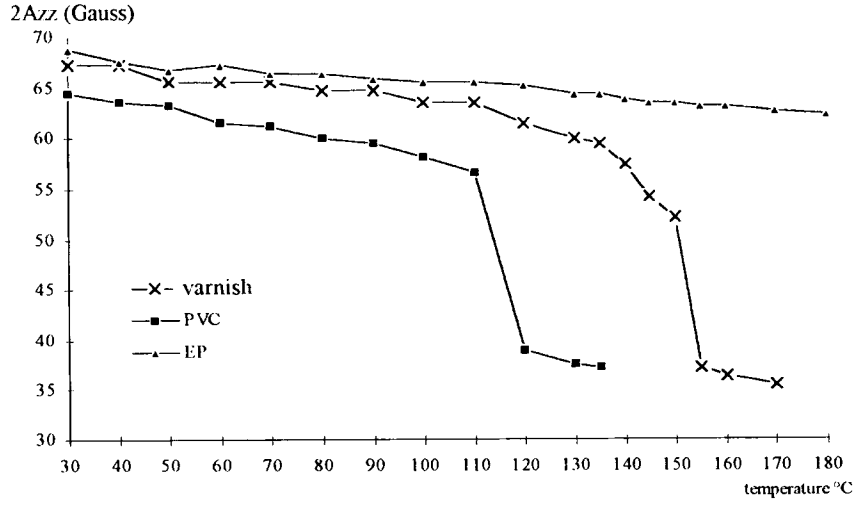


Figure 8 Evolution of the hyperfine split of probe **3** against the temperature at which the varnish, the PVC, and the EP phase are heated.

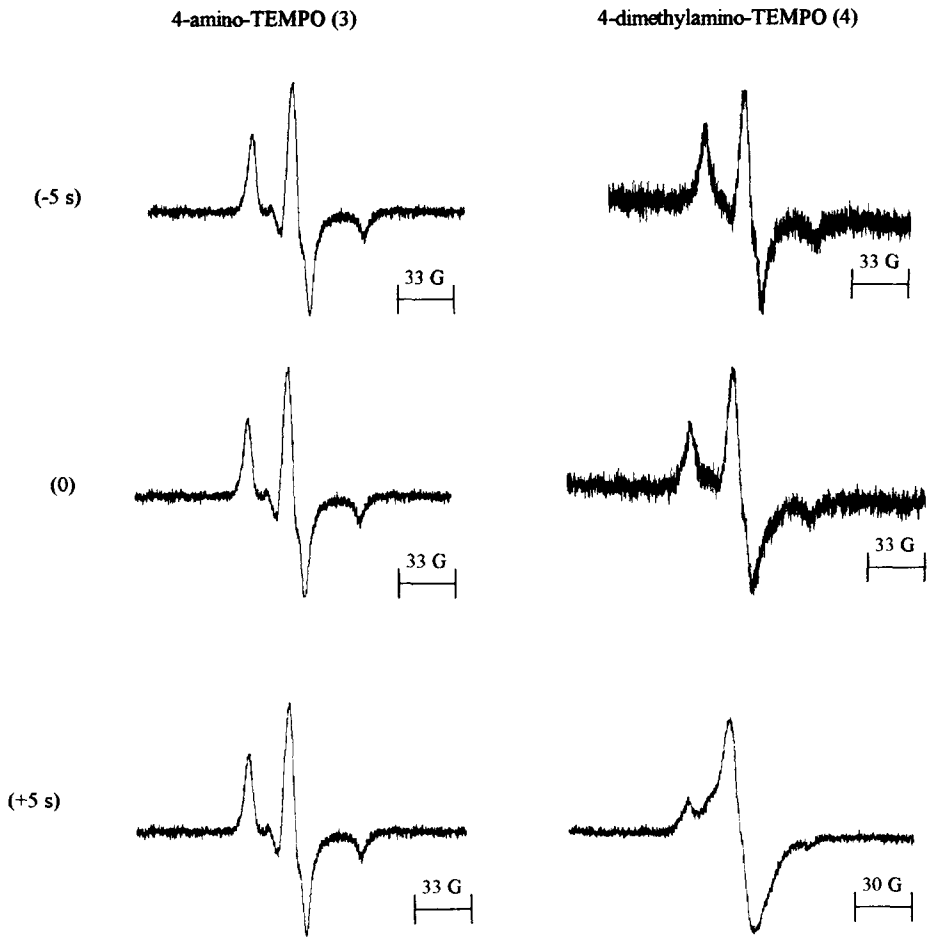


Figure 9 ESR spectra for probes **3** and **4**, for variously cured varnish: (−5 s) undercured, (0) normally cured, (+5 s) overcured.

The signal of 4-amino-TEMPO was always a hundred times more intense than those of other probes, although its volatility and molecular weight were close to that of 4-dimethylamino-TEMPO. This suggests that the 4-amino-TEMPO got grafted onto the polymer chains of the varnish during curing, for instance by reaction with C — Cl of PVC or with C — O of oxiranes:[14]

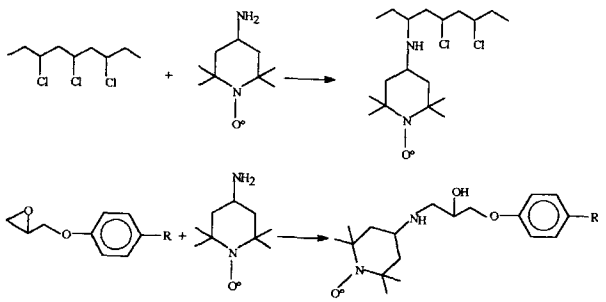


Table II T_g, T_{50G}, and T_{fs} Obtained for Different Cures of the Varnish

Cure	T_g (±1°C)	T_{50G} (±5°C)	T_{fs} (±5°C)
Undercured (−5 s)	68.4	146	132
Normally cured (0)	76.2	152	142
Overcured (+ 5 s)	82.1	>180[a]	>180

[a] Maximum temperature allowed by the instrument.

Reactions with carboxylic ending chains were also possible.

Aminoxyls have often been used to study transitions in polymers. When the temperature of analysis increases, the broad spectrum (2 Azz = 64 G) evolves to a narrow triplet (2 Azz = 36 G) after a rapid transition at 2 Azz = 50 G, often correlated to T_g. In general, the T_{50G} values are higher than the T_g values because they are measured at a fre-

Table III Comparison of T_{50G} and T_{fs} of 4-amino-TEMPO Incorporated in Different Materials

Temperature	PVC Phase of the Varnish	PVC Resin[15,16]	Extruded PVC Plates	Varnish
Incorporation temperatures (°C)	80	80	180	290
Transition temperatures (°C)	T_{50G} = 115	T_{50G} = 115	T_{50G} = 128–135[a]	T_{fs} = 132[b] T_{fs} = 142[c]

[a] Depending on the formulation of the PVC.
[b] Undercured varnish.
[c] Normally cured varnish.

quency 10^7 times higher.[17] 4-amino-TEMPO showed two types of transition in the vinylic organosol (above room temperature): T_{fs} and T_{50G}.

The spectrum at 145°C corresponded to the superposition of two signals: the lines A, B, and C (Fig. 4) and the lines D, B, and E. In the varnish, the probe was located in two environments reflecting the heterogeneity of the system. The T_{fs} value is always higher than its real transition temperature. This temperature could not be observed because there was an overlap of the lines of the fast signal (D, B, and E) and those of the second environment (lines A, B, and C). In undercured (T_{fs} = 132°C) and normally cured (T_{fs} = 142°C), varnish samples (Table II), T_{fs} was close to T_{50G} measured in PVC plates which had been processed at high temperature (T_g = 128–135°C)[9] (Table III). These transitions are characteristic of NO° groups bonding covalently to PVC. When the incorporation was made at 80°C, the 4-amino-TEMPO did not bond to the polymer: T_{50G} of 3 in the PVC component of the varnish (T_{50G} = 115°C) was close to that of the probe incorporated in a similar way in the PVC plates.[15,16]

The behavior of 4-amino-TEMPO showed that in the PVC and EP phases only one environment was observed by ESR. In the varnish, lines D and E were due to 4-amino-TEMPO in the PVC phase, while lines A, B, and C corresponded to 4-amino-TEMPO in the EP phase. The first transition (T_{fs}) was attributed to the PVC phase and the second transition (T_{50G}) to the EP phase. It was interesting to note that by ESR, the use of 4-amino-TEMPO probes enabled the observation of two transitions, whereas with DSC only one transition (T_g = 76°C) characteristic of PVC was observed.

The study of the varnish for various degrees of curing showed a marked effect on the transition temperatures, reflecting the structural changes of the polymeric network. In undercured varnish, T_g (Table II) was lower than in PVC (T_g = 80°C[2]). The PVC phase seemed to be plasticized by some constituents of the varnish. With a normal curing, T_g was close to that of the PVC. The compounds plasticizing PVC seemed to react during the polymerization, which suggested that they could be monomers. This could play an important role in the mechanical properties of the varnish. In overcured varnish, ESR showed a dramatic drop in the mobility of the polymeric chains of PVC responsible for the elasticity of the varnish (T_{50G} and T_{fs} over 180°C); the PVC chains were completely immobilized by the tridimensional network of EP.

CONCLUSION

The distribution of paramagnetic probes added to a varnish depended on their functional groups and their volatility. During the polymerization of the varnish at high temperature, TEMPO, 4-hydroxy-TEMPO, and 4-dimethylamino-TEMPO, without a primary amine group, evaporated. 4-amino-TEMPO was bonded covalently to each phase of the polymer through its primary amine group, which enabled the study of transitions in each phase. It was then possible to label an industrial polymer without previous modification. The transitions for various degrees of curing suggested the influence of reactive components (like monomers) of the varnish on its properties. The spectrum of the varnish is the sum of the spectra of the two phases of the varnish. Specific labeling of one phase will now make it possible to study of the influence of food simulants on the modifications of structures undergone by the varnish.

The authors wish to express their thanks to PECHINEY-CRV and the French Ministry of Industry for financial assistance. They also wish to express their gratitude to R. de Marco, P. Mortreuil, N. Thorne, A. Pichat, and M. Lebaigue (from PECHINEY-CRV) for their valuable suggestions and guidance. They would like to express their gratitude to the company Holden Europe (ICI Paints),

and especially to J. Guerrier and P. Hélias for their helpful suggestions, technical support, and the samples provided. Finally, they thank M. Hamdami for the synthesis and purification of 4-dimethylamino-TEMPO.

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Received December 7, 1995
Accepted May 30, 1996