

Development of Green and Dark Blue Colors in Epoxy Resins Cured with 4,4'-Diaminodiphenylmethane

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Synopsis

From a study of the oxidation of bisphenol-A epoxy resin cured with DDM (4,4'-diaminodiphenylmethane), it has been shown that the development of greenish-blue colors is due to an initial reaction between molecular oxygen and secondary amine groups. A full reaction scheme is suggested and supporting evidence, in the form of UV/visible, infrared, and ESR spectra, is presented.

INTRODUCTION

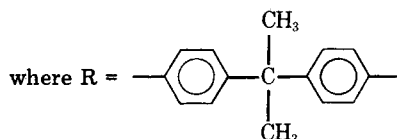
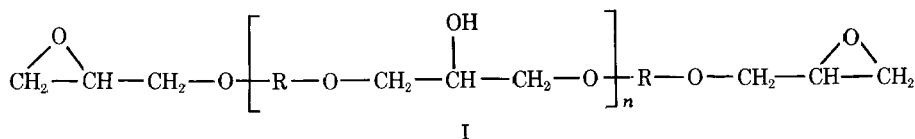
Normally cured bisphenol-A epoxy resins with DDM hardener are light brownish or amber in color. Green or dark blue colors may develop on exposure of such resins to sunlight or ultraviolet radiation. Similar colors may develop when these resins are heated in air. For instance, a disk used for the measurement of the dielectric properties of such a resin (Araldite MY750/DDM) between room temperature and 200°C was a dark blue color after completion of the measurements, although there was no significant change in the dielectric constant.¹ Some years ago it was observed that epoxy resins had weak ESR spectra,² which increased in intensity after irradiation with UV light. Evidence for the presence of unpaired electrons in epoxy resins has also been published by Ove-nall,³ but the composition and cure treatment is not specified. Recently the presence of a radical species in DDM-cured resins has been proposed, but no direct evidence for its formation was offered.⁴

In this paper we show that the oxidation of partially reacted DDM results in the development of a species with an absorption at 620 nm. A mechanism is proposed to account for the observed results.

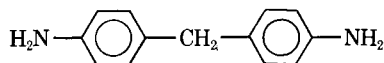
EXPERIMENTAL

The materials used in this work were all of commercial grade and used as supplied by the Ciba-Geigy Plastics and Additives Company. The epoxy resins

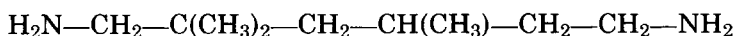
used were mixtures of compounds with Structure I:



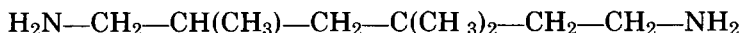
with an average value of n of about 0.2 or 1.7. The two resins were Araldite GY250 (epoxy content 5.24 mol/kg) and Araldite 6100 (epoxy content 2.10 mol/kg). GY250 consists largely of bisphenol-A diglycidyl ether, i.e., the compound in which $n = 0$ in Structure I. The resins were cured with either DDM, which has the structure



or TDM, which consists of equal parts of



and



Cured resin samples with a range of resin:hardener stoichiometries were prepared from both the 6100 and the GY250 prepolymers. Except for the TMD-cured sample, which was allowed to gel before curing, the resins were all given a standard cure treatment of 1 h at 110°C followed by 1 h at 140°C. The details of the formulation of the resins are given in Table I: for equivalent amounts of

TABLE I
Formulation of Cured Resins

Designation	Resin	Hardener	Amino-hydrogen atoms per epoxy group	Cure treatment
S1	GY250	DDM	1:1	1 h at 110°C + 1 h at 140°C
E1	GY250	DDM	3:2	1 h at 110°C + 1 h at 140°C
D1	GY250	DDM	3:4	1 h at 110°C + 1 h at 140°C
S2	6100	DDM	1:1	1 h at 110°C + 1 h at 140°C
E2	6100	DDM	3:2	1 h at 110°C + 1 h at 140°C
E3	GY250	TMD	3:2	Allowed to gel at 25°C 1 h at 110°C + 1 h at 140°C

epoxy groups and active hydrogen a molar ratio of hardener to resin of 1:2 is required. The resins were prepared as 2–3-mm-thick sheets, from which samples were cut and polished for visible spectroscopy; powdered samples of resins S1 and E1 were prepared to enable the relationship between the development of color and the ESR signal to be investigated.

The cured resins were subjected to a number of heat treatments under controlled atmospheres (air, nitrogen, oxygen), and these treatments are described in the Results and Discussion section of this report. The development of color was monitored using a Perkin-Elmer 137 UV/visible spectrometer. ESR spectra were collected using a Varian New Century E-line ESR spectrometer operating at 9.4 GHz, with field modulation of 100 kHz.

RESULTS AND DISCUSSION

In general it has been found that color develops more rapidly in some resins than in others. It was found that when the concentration of DDM hardener was in excess of that required to give a fully cured resin (E1, E2) green colors always developed readily when the resin was heated in air or oxygen. For example, E1 heated in oxygen at 90°C became green and an absorption band at $\lambda_m = 620$ nm developed [Fig. 1(a)]. However, color did not develop under these conditions in the fully cured resins (S1, S2) [Fig. 1(b)] or resins cured with a deficiency of DDM. The resin cured with an excess of the aliphatic hardener TMD showed no color development when heated in oxygen at 90°C. By control of the environment it was established that color development was inhibited in a nitrogen atmosphere. Thus, color formation appears to be due to the reaction between molecular oxygen and unreacted amine groups on the DDM units. If this is the case, the rate of color formation should depend on the diffusion of oxygen into the resin. For a diffusion-controlled oxidative reaction leading to the formation of a chromophore the absorbance should be a linear function of the square root of the reaction time, provided that Beer's law ($A = \epsilon cl$) holds: as shown in Figure 2, this is in fact the case. The positive intercept should not be interpreted as evidence that there is an induction period, since similar intercepts on the time axis are often observed in simple diffusion experiments. Further evidence that the reaction is controlled by diffusion into the resin was provided by cutting a section through one of the colored test specimens: It was obvious that the highest concentration of chromophores was at the surface of the sample. By successively polishing away the surface of the sample, it was possible to obtain a rough concentration—depth profile for the color centers as shown in Figure 3. As the extinction coefficient ϵ of the chromophores is not known; only relative measurements of the concentration c are possible.

A further observation of interest was that if a highly colored resin sample was heated to 140°C in oxygen or nitrogen, the green color faded over a period of 15 min and the resin became straw colored.

The results outlined above are summarized in Table II.

It has been observed that DDM-cured epoxy resins that have been exposed to ultraviolet radiation (mercury lamp) are greenish-blue in color, and weak ESR spectra have been recorded showing that these resins contain long-lived radicals.²

The effects of thermal treatments in an oxygen atmosphere on the ESR spectra

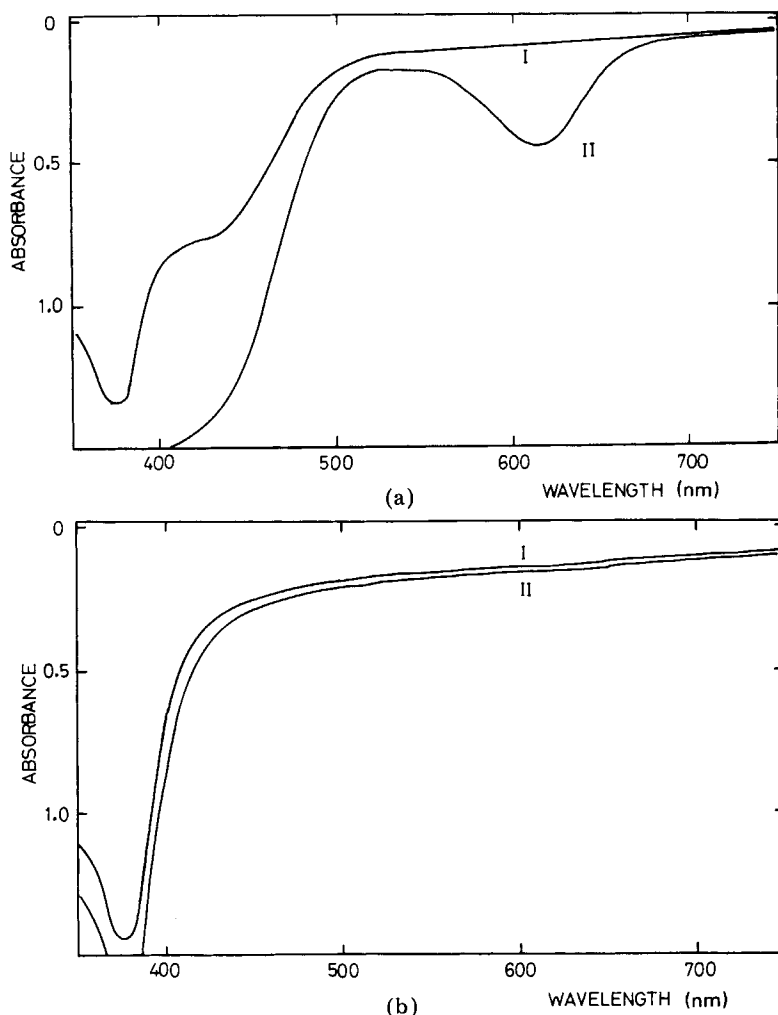


Fig. 1. (a) Visible region spectra of resin cured with excess DDM: (I) original cured resin before treatment; (II) after heating for 18 h in oxygen at 90°C. (b) Visible region spectra of resin cured with the stoichiometric concentration of DDM: (I) original cured resin before treatment; (II) after heating for 18 h in oxygen at 90°C.

of resin GY250 cured with excess DDM, E1, have been investigated systematically. Recently cured (1–2-day-old) resin had a minimal ESR spectrum which was barely detectable, showing that the concentration of free radicals was extremely low. After heating this resin for 18 h in a nitrogen atmosphere at 90°C, there was no increase in the concentration of radicals; the spectrum was unchanged after an additional heat treatment of 30 min at 140°C. A sample heated in an oxygen atmosphere for 18 h at 90°C developed the ESR spectrum shown in Figure 4(a), and the resin became greenish-blue in color. Treatment of a sample with this greenish-blue color (after treatment for 18 h at 90°C in oxygen) in nitrogen at 140°C for 30 min caused the color to change to a light yellow-brown. However, the ESR spectrum of the resin is essentially unchanged [Fig. 4(b)]. Thus the short-term treatment at 140°C is not sufficient to allow the radical centers to be destroyed by further reaction with oxygen. A sample of resin cured

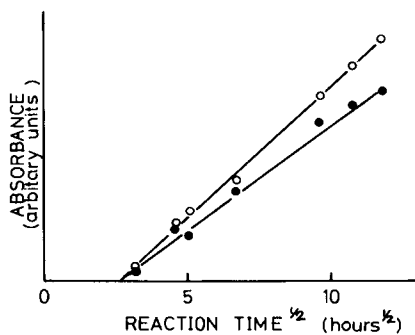


Fig. 2. Development of the absorption at 620 nm during heating in oxygen at 90°C: (O) resin EI; (●) resin with molar ratio of DDM:GY250 of 2.5:4.0.

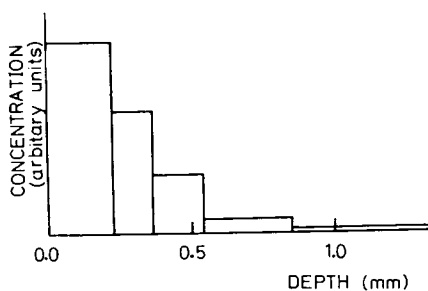


Fig. 3. Histogram of concentration, in arbitrary units, vs. depth for a 2.8 mm thick sample of EI after heating in air at 90°C for 18 h.

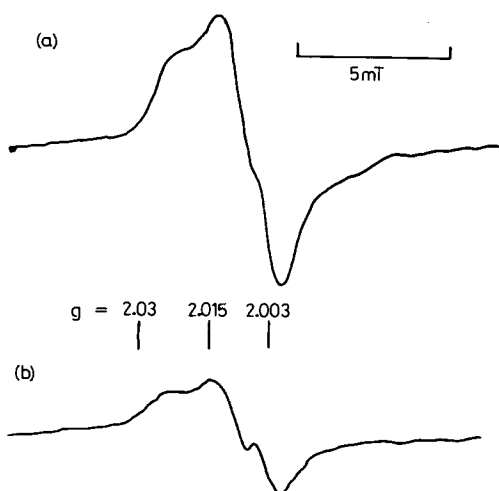


Fig. 4. ESR spectra: (a) EI after heating for 18 h in oxygen at 90°C; (b) EI after heating for 18 h in oxygen at 90°C + 30 min in nitrogen at 140°C. The spectrometer settings were identical for the two samples.

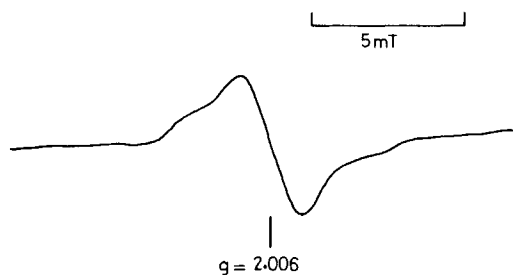


Fig. 5. ESR spectra of a resin cured with the stoichiometric concentration DDM, S1, after heating for 18 h in oxygen at 90°C. Sample size and instrument settings were such that the spectrometer sensitivity was about 2.5 times that used for the spectra of Figure 4.

with the stoichiometric concentration of DDM, S1, on heating in an oxygen atmosphere for 18 h at 90°C has a weaker ESR spectrum [Fig. 5] with a g value of 2.006 which is the same as that reported by Ovenall.³ Therefore, the spectra shown in Figure 4 are due to an oxidation product of the excess unreacted amine. The spectra in Figure 4 are due to the presence of at least two radicals so that assignment is difficult; however, the presence of a peroxy radical may be indicated. For these radicals somewhat variable g values have been reported, but typical values⁵ are $\langle g \rangle \sim 2.015$ with $g_{\parallel} \sim 2.03$ and $g_{\perp} \sim 2.003$.

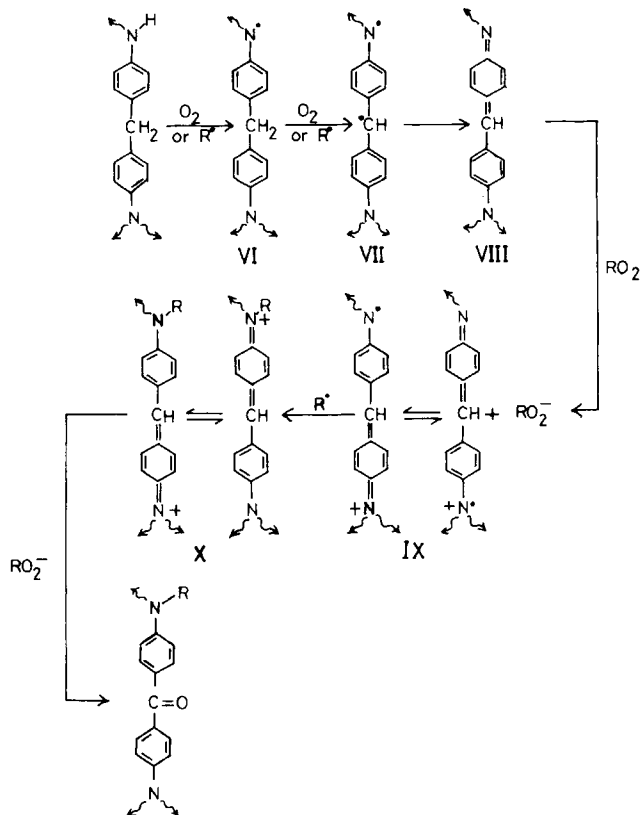
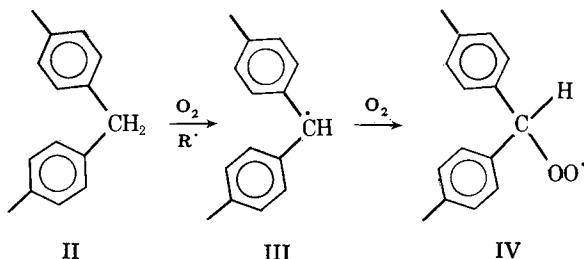


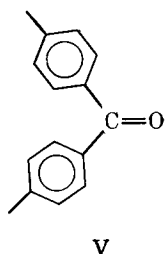
Fig. 6. Reaction scheme for the formation of color in epoxy resins cured with excess DDM.

Reactions of DDM-Cured Epoxy Resins with Molecular Oxygen

In a resin cured with the stoichiometric amount of DDM, oxidative attack takes the form of hydrogen abstraction from the methylene group in the DDM residue II; stabilization of the radical by delocalization of the free electron makes this an easier reaction than abstraction from an aliphatic chain:



The formation of such a species has been postulated in the oxidation of Friedel-Crafts type thermally stable polymers with the eventual formation of a carbonyl group,⁶ V:



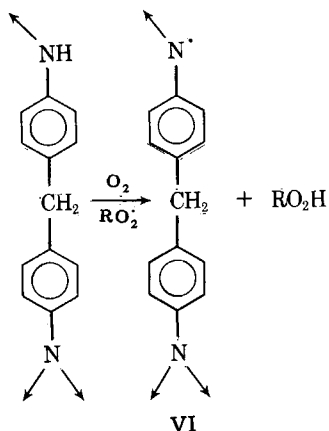
Although the specific route for the formation of V is not established, the radicals III, or more probably IV, may be relatively stable in a rigid epoxy resin at room temperature; hence this is the radical that results in the spectrum shown in Figure

TABLE II
Summary of Results

Treatment Resin	18 h at 90°C in O ₂		18 h at 90°C in N ₂		18 h at 90°C in O ₂ + 15 min at 140°C in N ₂	
	Visible spectrum	ESR spectrum	Visible spectrum	ESR spectrum	Visible spectrum	ESR spectrum
S1	yellow	weak	yellow	—	yellow	weak
E1	green— λ _m 620 nm	strong	yellow	none	yellow	strong
D1	yellow	—	yellow	—	—	—
S2	yellow	—	yellow	—	—	—
E2	green— λ _m 620 nm	—	yellow	—	—	—
E3	yellow	—	yellow	—	—	—

5. The development of a carbonyl band at 5.8μ similar to that reported by Conley and Dante⁷ was observed in the IR spectra of these resins during the thermal treatments described above. Such an oxidation is slow, as would be expected from the stability of epoxy resins, and does not lead to the formation of colored species within the time scale of the present experiments. Similar considerations will apply to the resins cured with less than the stoichiometric amount of hardener, only there will be some unreacted epoxy end groups present.

Resins cured with an excess of hardener may contain both unreacted primary and secondary amine groups. However, in the discussion below, only secondary amine groups will be considered since, as the rate of reaction of secondary amine is only about 0.15 times that of the primary amine groups,⁸ they will be present in a much higher concentration. Aromatic amines are commonly used as antioxidants as the hydrogen atoms on the amine groups are labile and readily "extracted" by free radicals.⁹ It is possible for direct attack of oxygen onto an antioxidant molecule to occur, and for residual secondary amine groups in the epoxy network the reaction would be



It is possible that VI is the radical that is responsible for the strong ESR signal that results from the oxidation of these resins. Alternatively, further reaction could occur so that a more stable peroxy radical is formed.¹⁰

From the results outlined in Table II it is apparent that the unreacted amine groups are involved in the color formation: We propose that VI is a precursor to the formation of a colored species. A possible reaction scheme that explains the observed results is given in Figure 6. The first step is the removal of the hydrogen atom from the secondary amine group, this is followed by the abstraction of a hydrogen atom from the methylene which leads to VIII, possibly through the transient biradical intermediate VII. There is no reason to expect that any of the species formed up to this point in the scheme will be colored, but they would account for the increased UV absorption [Fig. 4(a)]. Further reaction of VIII is possible with the formation of species IX and X, which are directly analogous to the so-called Wursters salts¹¹ and could well have an absorption in the 600-nm region. Formation of a Wursters salt from the antioxidant tetramethylphenylene diamine has been reported by Boozer and Hammond¹²: It

is interesting to note that on complete oxidation of the tetramethylphenylene the blue color of the salt was lost, and this was attributed to hydrolysis of the salt. However, from our experiments a more likely candidate for the decolorization reaction in epoxy resin systems would seem to be the neutralization of the cation by reaction with a peroxy anion. Such a reaction would lead to the formation of a carbonyl group, as shown in the last step of the scheme given in Figure 6. Such a mechanism is consistent with the decolorization occurring without the destruction of the radical centers responsible for the ESR spectra.

It is possible that the TMD-cured resin could undergo some similar reactions, but due to the structure of the hardener molecule no colored species can be formed.

In conclusion, it is important to note that DDM-cured bisphenol-A epoxy resins are relatively stable at elevated temperatures in the region of 150°C for considerable periods. The changes that we observed are the initial stages of the degradation process and are only detectable due to the sensitivity of both UV/visible and ESR spectroscopy. After measurement of the elastic modulus of these resins following several cycles of treatment at elevated temperatures, it was not possible to detect significant structural change. Color development in "normally" cured epoxy resins is often very variable; the present results show that its rate will be dependent on the concentration of hardener. If required, it is possible that the formation of such colors could be used as a diagnostic test for exhaustive cure or the "goodness" of mixing.

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