Photooxidation of Amine Crosslinked Epoxies
I. The DGEBA–DDM System

V. BELLENGER and J. VERDU, *Département Matériaux, E.N.S.A.M.,*
151 Boulevard de l'Hôpital, 75640 Paris Cedex 13, France

Synopsis

The photooxidation in the solar UV range of tridimensional networks based on the diglycidyl ether of bisphenol A (DGEBA) and diaminodiphenyl methane (DDM) is characterized by the formation of carbonyl, amide, and hydroperoxide groups and by at least two types of chromophores. One absorbs strongly in the near UV, violet, and blue regions, and is responsible for the development of an internal screening effect leading to a decrease of photooxidation rate during exposure. The other, which absorbs in the red region (λ_{max} = 615 nm), is responsible for the green color of oxidized samples and is derived from the oxidation of the diamine bridge. The influences of hardener concentration and thermal treatments are explained in terms of a stabilizing effect of unreacted DDM molecules and a photoinitiating effect of some thermal-oxidation products, presumably hydroperoxides.

INTRODUCTION

Despite the practical interest in epoxy systems in high performance composites, little has been published on their photodegradation and photooxidation mechanisms. The available weathering data, however, show that exposure to ultraviolet radiation induces crack formation on exposed surfaces[1] and erosion of superficial layers by atmospheric agents,[2] showing the existence of an efficient skeleton breaking process. Infrared spectroscopy (essentially Fourier transform method[2,3]) has mainly been used to monitor the structural changes, with particular attention paid to the buildup of oxygenated groups. Carbonyl groups are observed in all systems.[2-4] Their formation is photosensitized by structures coming from a previous thermal oxidation (for instance during cure treatments).[2,4] Hydroxyl and peroxide groups also accumulate in networks based on ether bridges, in which the tertiary hydrogen near the oxygen atom could be an important "weak point." Norrish-type reactions on carbonyl groups are assumed to be responsible for the skeleton breaking processes,[3] which are observed by DSC[2,4] and other thermal methods,[2] showing a decrease in T_g and/or in volatile yield in pyrolysis.

An interesting feature of the amine cured systems is the presence of an IR band at 1650–1670 cm^{-1}, which has received many assignments including double bond[5] or conjugated carbonyl structure.[6] We have previously shown that this structure is more probably an amide resulting from an oxidative attack of the methylene in α position of the nitrogen atom, as shown by the correlation between amide yield and initial concentration of α methylenes in nonaromatic amines.[4] From a practical point of view, these very hydrophilic structures can play an important role in the deterioration processes, acting as "sensitizers" in the microcracking due to swelling stresses.[7]

The aim of this paper is to describe the photooxidation in the near UV range, of tridimensional polycondensates based on diglycidyl ether of bisphenol A (DGEBA), crosslinked by diaminodiphenyl methane (DDM).

EXPERIMENTAL

Materials. DGEBA has an epoxide index of 5.40 mol·kg^{-1} corresponding to a DP$_n$ of 0.11. DDM:

$$H_2N-\langle O \rangle-CH_2-\langle O \rangle-NH_2$$
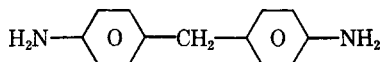
gives only one peak in GPC (tetrahydrofurane, microstyragel 100 Å, refractometric detection). For this study, we used the previously described approach based on thin films, (10–100 μm) polycondensed from solutions on a clean mercury surface.[4] The basic thermal treatment (2 h at 105°C followed by 1 h at 165°C), leads to a T_g of 436 ± 2K for the samples having the stoichiometric amine concentration. No evidence of incomplete cure was observed in the DSC traces.

Spectrophotometric Study. The UV-visible (Varian 635 D) and infrared spectra (Perkin-Elmer 580) were recorded in transmittance. For quantitative measurements, we used the peak at 1885 cm^{-1} as internal standard (absorbance per thickness unit: 23.0 ± 2.6 cm^{-1}). The results are expressed in absorbance unit per cm thickness (cm^{-1}). To evaluate the absolute quantum yields of amide formation, we previously measured the absorptivity of the

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peak of a model compound: acetanilide in a cast PVC film. Amide concentrations can thus be deduced from the peak absorbance at 1670 cm^{-1} using an ϵ value of 470 kg·mol^{-1}·cm^{-1}. The quantum yields of carbonyl formation are derived from ϵ values found in the literature.[8] We took ϵ = 200 kg·mol^{-1}·cm^{-1} at 1730 cm^{-1}.

Hydroperoxides are determined by the Zeppenfield method[9] modified by Petruj et al.,[10] using the thiocyanate $-Fe^{++}$ complex.

Photochemical Study. The reactor is equipped with a fluorescent lamp (Philips TL05) emitting only in the solar UV range (300–450 mm with the maximum at 365 nm). o-Nitrobenzaldehyde actinometry[11] gave an intensity of 3.5 × 10^{15} photon cm^{-2}·s^{-1} at sample level. The temperature was 31 ± 1°C; the films were exposed to air.

RESULTS

Common Features of All Systems under Study

The photochemical behavior of all samples based on DGEBA–DDM polycondensates in characterized by:

(a) The buildup of carbonyl (1730 cm^{-1}) and amide (1670 cm^{-1}) peaks (Fig. 1). The kinetics are more or less autoretarded, depending on stoichiometry, thickness, or thermal treatment (see below). Typical values of initial rates and corresponding values of quantum yields are given in Table I.

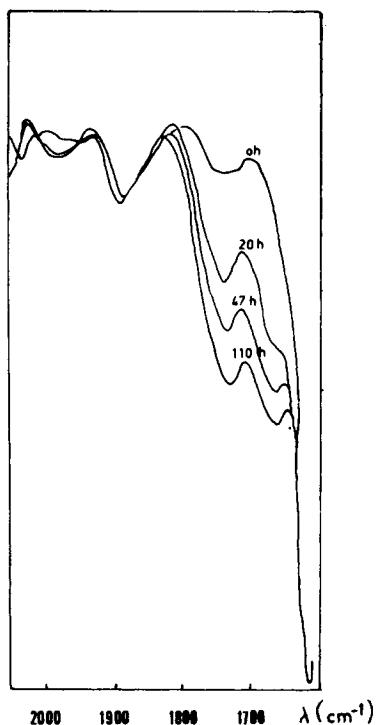(b) The development of a green color due to a chromophore absorbing at 615

Fig. 1. Infrared spectra at various exposure times (film of 24 μm thickness, with stoichiometric concentration of DDM and basic thermal treatment).

nm.   The absorption in near UV, violet, and blue regions also increases strongly (Fig. 2).

(c) Hydroperoxide formation: The POOH concentration increases during the early days of exposure, reaches a maximum, and then decreases slowly to a photostationary state (Fig. 3).   Typical values of quantum yields are given in Table I.   It is interesting to note that the chemical treatment needed for POOH determination develops an intense green color due to a strong increase of the absorption at 615 nm.   We verified that iron chloride is responsible for this phenomenon.   In Figure 3, we plotted the absorbances at 615 nm before and after POOH determination vs. exposure time.

Influence of Thickness on Photooxidation Kinetic

We compared the behavior of 13 films differing only in their thicknesses (between 25 and 85 μm).   The results of carbonyl determination after various times of exposure are given in Figure 4.   It is clear that the efficiency of the autoretardation process increases with the film thickness.   We shall also note a noticeable influence of thickness on initial rate (Fig. 5).

Influence of Stoichiometry

We compared the kinetic curves of carbonyl and amide formation for samples crosslinked with respectively 75%, 100%, and 125% DDM with respect to the

TABLE I
Initial Rates and Quantum Yields for Carbonyl, Amide, and Hydroperoxide Formation

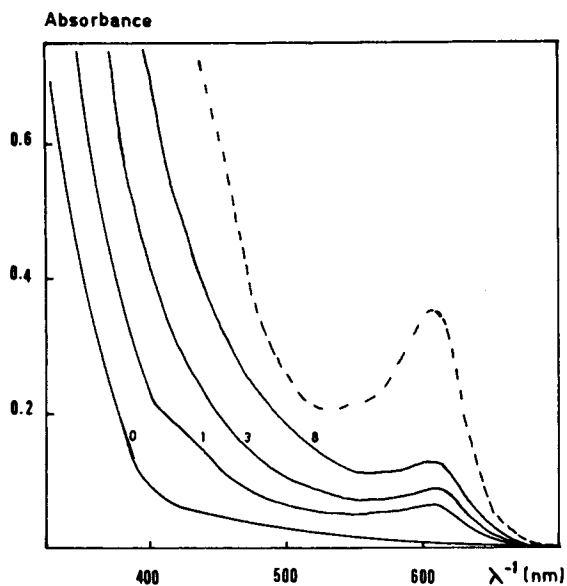| Thickness (μm)	r_{CO} (absorbance units·cm^{-1} thickness·h^{-1})	ϕ_{CO} (molecules/photon absorbed)	r_A (absorbance units·cm^{-1} thickness·h^{-1})	ϕ_A (molecules/photon absorbed)	r_{POOH} (mol·kg^{-1}·h^{-1})	ϕ_{POOH} (molecules/photon absorbed)
32 ± 8	0.44 ± 0.048	4 × 10^{-4}	0.31 ± 0.05	1.21 × 10^{-4}	0.89 × 10^{-4}	2.3 × 10^{-5}

Fig. 2. UV visible spectra for various exposure times.   Exposure times (days) are indicated on the figure.   The dotted line corresponds to the film aged 8 days after treatment by iron chloride.

stoichiometric value.   Figures 6 and 7 reveal a complex influence of the stoichiometry.   We shall essentially note two results: (i) the incompletely crosslinked sample (75% DDM) is the least stable; (ii) the autoretarded behavior is especially noticeable in the sample containing an excess of DDM.
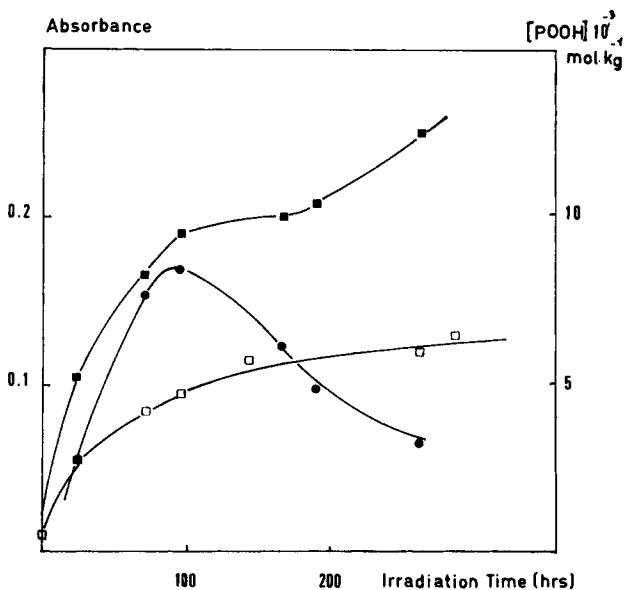
Fig. 3. Changes in hydroperoxide concentration ($\bullet$) and absorbance at 615 nm before ($\square$) and after ($\blacksquare$) chemical treatment during UV exposure.
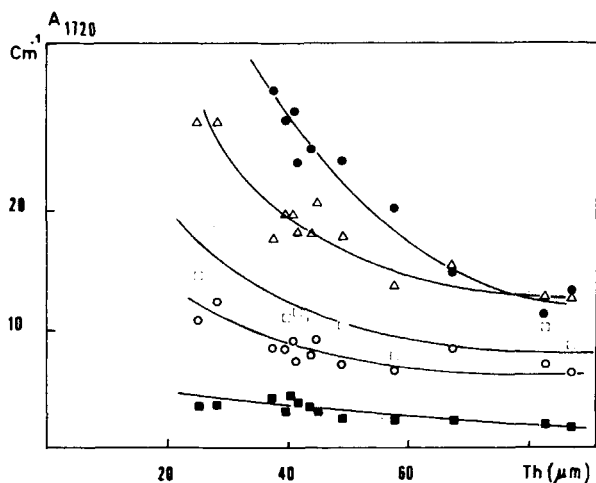
Fig. 4. Intensity of the carbonyl peak after various exposure times against film thickness: (■) 0 h; (O) 24 h; (□) 47 h; (△) 119 h; (●) 166 h.

Influence of Thermal Treatments

Six samples of the same thickness (25 μm) were obtained after only 2 h of thermal treatment at 105°C in air. The cure was finished under the following conditions: 0.5, 1, or 2 h at 160°C in air or 0.5, 1, or 2 h at 160°C in vacuum (1 mm Hg). From kinetic curves of amide and carbonyl buildup, we took initial (r_i) and "stationary" (taken between 100 and 150 h of exposure) rates (r_s). The same treatment was applied to the absorbance changes at 500 nm. The results are summarized in Table II, which calls for the following comments:

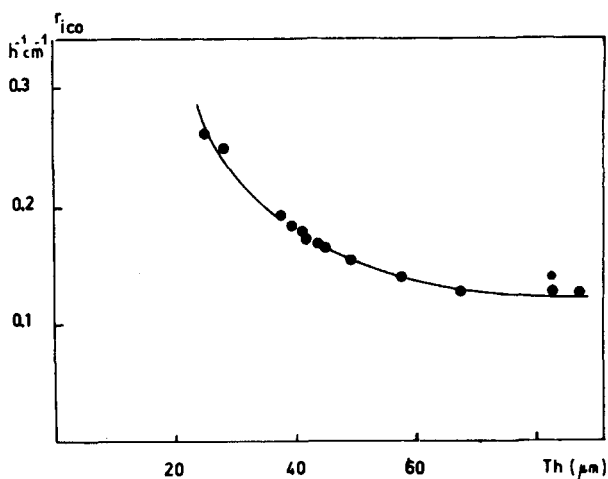(a) The thermal treatment in vacuum does not significantly influence the photochemical behavior.

Fig. 5. Initial rates of carbonyl growth against film thickness.
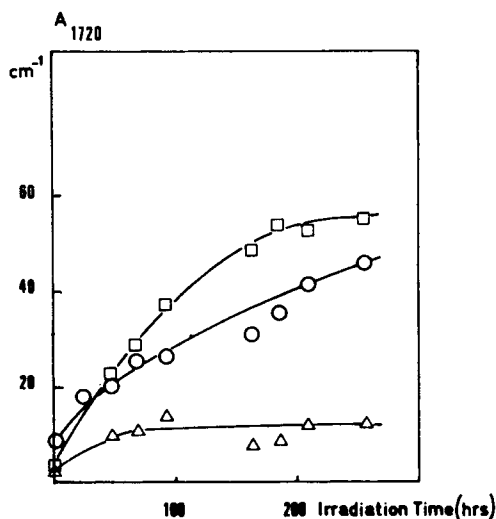
Fig. 6. Carbonyl growth in films differing by DDM concentration: (□) 75% DDM; (▲) 125% DDM; (○) 100% DDM.

(b) The thermal treatment in air results in initial rates noticeably higher than those obtained on samples treated in vacuum, but the autoretarded character of the kinetics is also strongly enhanced so that the long-term stability (taking our spectrophotometric criteria) is higher for samples treated in air than for samples treated in vacuum.

(c) The autoretardation is more pronounced for formation of amide and visible chromophores than for carbonyl groups.
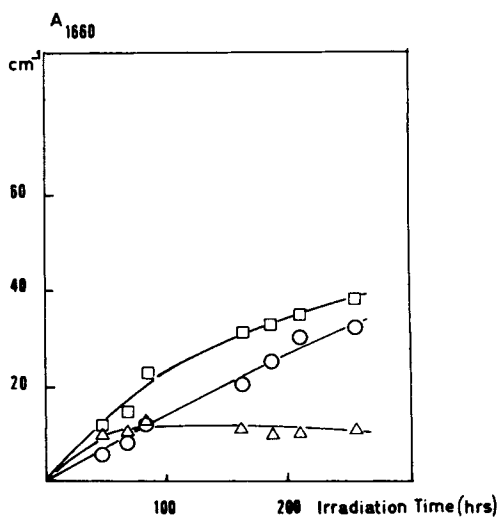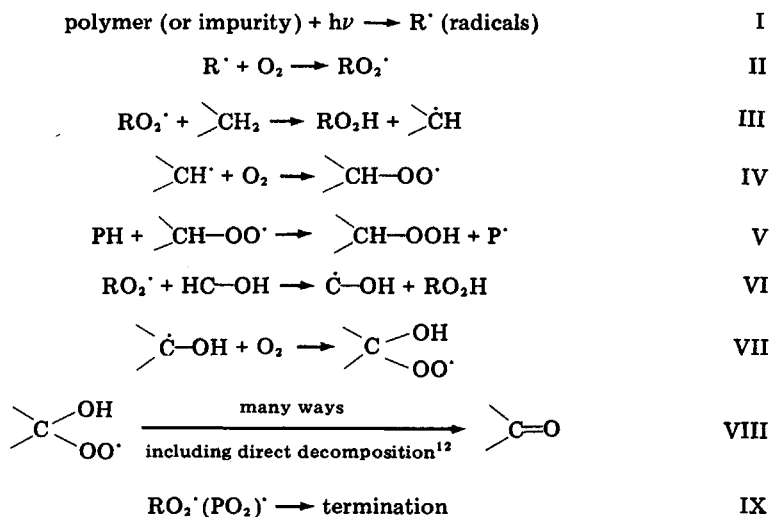

Fig. 7. Amide growth in films differing by DDM concentration (□) 75% DDM; (○) 100% DDM; (▲) 125% DDM.

TABLE II

Initial and "Stationary" Rates for Carbonyl Peak: $r_{i,CO}$ and $r_{s,CO}$, Amide Peak $r_{i,A}$ and $r_{s,A}$ and Absorbance at 500 mm: $r_{i,v}$ and $r_{s,v}$ $(cm^{-1} \cdot h^{-1})$

| Samples treated	$r_{i,CO}$	$r_{s,CO}$	$r_{i,CO}/r_{s,CO}$	$r_{i,A}$	$r_{s,A}$	$r_{i,A}/r_{i,A}$	$r_{i,v}$	$r_{s,v}$	$r_{i,v}/r_{s,v}$
In air (0.5 h)	0.51	0.06	8.5	0.40	0.00	$\gg 1$	1.25×10^{-3}	0	$\gg 1$
In air (1 h)	0.49	0.05	9.8	0.37	0.00	$\gg 1$	2.43×10^{-3}	0	$\gg 1$
In air (2 h)	0.30	0.20	1.5	0.36	0.16	2.25	2.25×10^{-3}	0.31×10^{-3}	7.26
In vacuum (0.5 h)	0.29	0.20	1.45	0.24	0.21	1.14	1.77×10^{-3}	0.35×10^{-3}	5.06
In vacuum (1 h)	0.36	0.13	2.77	0.27	0.27	1.00	1.88×10^{-3}	0.53×10^{-3}	3.55
In vacuum (2 h)	0.33	0.20	1.65	0.22	0.20	1.10	1.75×10^{-3}	0.39×10^{-3}	4.49

DISCUSSION

As previously shown,[4] the structural changes can essentially be discussed in terms of photoinitiated radical oxidation:

$$\text{polymer (or impurity)} + h\nu \longrightarrow R^{\cdot} \text{ (radicals)} \qquad \text{I}$$

$$R^{\cdot} + O_2 \longrightarrow RO_2{}^{\cdot} \qquad \text{II}$$

$$RO_2{}^{\cdot} + {>}CH_2 \longrightarrow RO_2H + {>}\dot{C}H \qquad \text{III}$$

$${>}\dot{C}H + O_2 \longrightarrow {>}CH{-}OO^{\cdot} \qquad \text{IV}$$

$$PH + {>}CH{-}OO^{\cdot} \longrightarrow {>}CH{-}OOH + P^{\cdot} \qquad \text{V}$$

$$RO_2{}^{\cdot} + HC{-}OH \longrightarrow \dot{C}{-}OH + RO_2H \qquad \text{VI}$$

$$\underset{/}{\overset{\backslash}{>}}\dot{C}{-}OH + O_2 \longrightarrow \underset{/}{\overset{\backslash}{>}}C{\overset{-OH}{\underset{-OO^{\cdot}}{}}} \qquad \text{VII}$$

$$\underset{/}{\overset{\backslash}{>}}C{\overset{-OH}{\underset{-OO^{\cdot}}{}}} \xrightarrow[\text{including direct decomposition}^{12}]{\text{many ways}} \underset{/}{\overset{\backslash}{>}}C{=}O \qquad \text{VIII}$$

$$RO_2{}^{\cdot} (PO_2)^{\cdot} \longrightarrow \text{termination} \qquad \text{IX}$$

Specific mechanisms of aromatic structures: quinone formation, photo-Fries rearrangements, etc. must be added to this scheme to explain chromophore formation and autoretardation effects.

The nature of photosensitizing species will be discussed elsewhere.[13] We shall note only the influence of a thermal treatment in air on initial rates (Table II) which can be interpreted in terms of photoinitiation by the products of a thermal oxidation of the polymer, presumably hydroperoxides.

Concerning propagation, it is interesting to note that four sites are mainly involved in hydrogen abstraction (reactions II and VI).
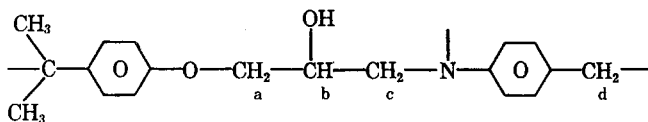
a, b, and d lead to carbonyl or carboxyl groups whereas c leads to an amide group. In the early days of exposure, approximately 18 carbonyl groups and 5 amide groups are found per POOH unit (Table I); we can therefore conclude that the hydroperoxides are readily decomposed to give more stable species. We previously suggested that the main source of carbonyls is the secondary alcohol. (Process VI → VIII).[4] In the system under study we could expect an easy hydrogen abstraction on the hardener methylene bridge (d), but the fact that the carbonyl peak is centered at 1730 cm^{-1} seems to indicate that the predominant species are nonconjugated CO groups essentially resulting from the attack on sites a and b.

In incompletely crosslinked samples (such as DDM 75%), the residual epoxide groups can also be a source of carbonyl groups. On the other hand, an enhanced macromolecular mobility favors "intermolecular" propagation of radical chains in these systems; this could explain their relatively high rates of oxidation.

Concerning the color development, many causes can be involved:

(i) Formation of quinonic structures derived from an oxidative attack of aromatic structures, as observed in practically all polymers containing the benzene ring.[14]

(ii) Formation of nitroxyl radicals.

(iii) Formation of a particular chromophore absorbing selectively at 615 nm. It is clear that this last structure results in hydroperoxide decomposition as shown by the effect of iron chloride whose catalytic influence on this process is well known.[15] The fact that this chromophore appears only in DDM systems[13] seems to indicate that an oxidative attack of the methylene bridge is involved in its formation:

chromophore containing probably the benzophenone structure
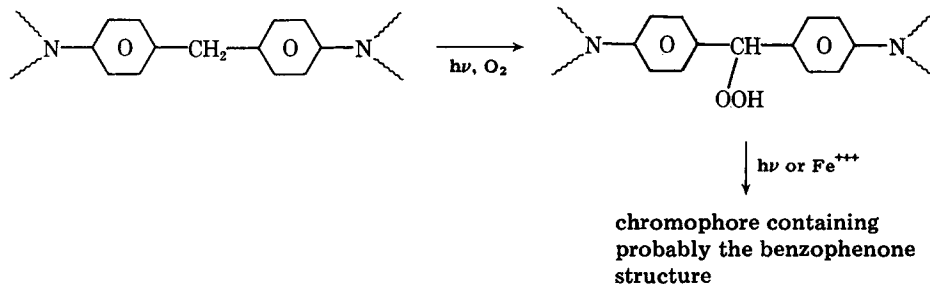
Such a structure could have a very high absorptivity at 615 nm so that traces indetectable by IR may have a significant influence on color development.

The strong increase of near UV absorption results in an internal screen effect responsible for the behavior observed in Figure 4 and probably the decrease of hydroperoxide concentration observed in Figure 3. The fact that the chromophores, which appear, are distributed across the thickness, according to the Beer–Lambert law, easily explains the increase in autoretardation effect with film thickness.

It is, however, difficult to attribute to this mechanism the fact that the reaction is completely stopped in films of higher thicknesses; on the other hand, the initial rates also decrease with thickness (Fig. 5), which cannot be explained by the development of a screen effect during exposure. It seems, therefore, that another autoinhibiting mechanism operates as soon as the photooxidation begins. Some interesting data can be derived from Table II.

For films having the same thickness and approximately the same initial UV

absorption, the rate lowering during exposure is considerably higher in films treated in air than in films treated in vacuum, as shown by the ratios r_i/r_s, which can represent the efficiency of the autoinhibiting phenomenon. We can therefore summarize its features as follows: (i) an increase with thickness; (ii) a decrease with thermal treatment in vacuum; (iii) also a decrease with a long thermal treatment in air (see table II).

The simplest hypothesis which comes into mind is that this phenomenon is due to the presence of low molecular weight compounds which remain partially trapped in the tridimensional network and which are easily eliminated when outgassing conditions are favorable (i.e., thin films and/or heating in vacuum).

It remains to identify these compounds. The GPC of tetrahydrofuran extracts (at ambient temperature for 1 day), displays only one peak having the same retention volume as DDM. On the other hand, we observe a particularly marked autoretarded behavior in samples containing an excess of DDM (Figs. 6 and 7). It seems, therefore, that the nonreacted DDM molecules are responsible for the inhibiting effect. It is well known that amines are good antioxidants, but our kinetic data, and essentially the influence of a previous thermal oxidation, favor a stabilizing effect of an oxidation product of DDM rather than DDM itself. Stable nitroxyl radicals, for instance, could be involved.

We can therefore conclude that the photooxidation of DGEBA–DDM polycondensates is a very complex process, involving the presence of two main oxidative chains (probably competitive), leading to carbonyl and amide groups, respectively.

The amine group seems to be the main source of chromophores.

The accumulation of these chromophores leads to an internal screen effect, limiting the photodegradation to layers of some dozens of micrometers thick. The importance of some low molecular compounds, presumably nonreacted amine, in the inhibition process is such that the photochemical behavior depends noticeably on processing conditions.

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