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Effect of UV radiation on photolysis of epoxy maleate of bisphenol A

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Abstract

The behavior of unsaturated polyesteric resin epoxy maleate of bisphenol A (EMBA) to UV was investigated using both infrared (IR) and optical microscopy (OM) techniques. The UV radiation produces important modifications of the EMBA sample. A photodegradation process takes place by a free radical mechanism and involves both photolysis and photodegradation reactions. In the early stage of photolysis, the excitation of the double bonds of EMBA sample takes place with formation of radicals. The radicals, by combination, form some cross-linked structures. These structures undergo secondary reactions with hydroperoxide formation. The splitting of the EMBA chains initiated by hydroperoxide compounds leads to new aromatic and etheric structures, with elimination of both CO and CO_2.

Keywords: UV radiation; Epoxy maleate; Photodegradation; Mechanism

1. Introduction

Epoxy resins (ERs) are commercially available for more than four decades having some unique properties, including outstanding adhesion to most surfaces, high mechanical strength and chemical resistance [1,2]. Currently, about half of all ERs produced are used for surface coating applications. The rest is widely used in electrical and electronic industry, aerospace and building constructions and as resin matrices for advanced composites.

Cross-linked ERs are used as the matrix polymers of high performance composite materials, but such resins are brittle and have poor resistance to the crack propagation [3–5]. To meet required end-use performance, ERs are modified entering into combination with other polymers, or chemical compounds. The combination of ERs with synthetic and natural polymers can lead to blends and/or interpenetrating polymer networks (IPNs) [6–9]. The modification of ERs with acrylic acids produce vinyl ester resins [10–12], while the modification with anhydrides yields unsaturated polyester resins [6,13]. The last, with reactive carbon–carbon double bonds located in the backbone of the chain, are the advanced materials used in reinforced plastics, especially.

In our previous works, an unsaturated polyester resin, respective epoxy maleate of bisphenol A (EMBA), was used as the component part on synthesis of polyurethane (PU)-EMBA blends [6], as well as PU-EMBA semi-IPNs [7]. The synthesized semi-IPNs showed high mechanical properties and good thermal properties [14]. Under UV radiations up to 10 h exposure time the mechanical properties of the synthesized semi-IPNs were improved. In contrast, for the PU-EMBA semi-IPNs exposured to long time of irradiation (up to 200 h) photooxidative degradation took place with almost a total destruction of the raw structures [15]. It was remarked that to better understanding the effect produced by UV radiations upon the tested interpenetrating networks, it is obviously necessary to know the behavior of the network components to the UV radiations. If PU was extensively studied regarding its behavior to the UV radiations [16–19] there are no data published on the effect of UV radiations on the EMBA resins. Generally, the photodegradation of polyesters involves both photolysis and photo-oxidative reactions with extensive chain scission and cross-linking reactions. Predominately, these reactions lead to the formation of

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gaseous products (CO and CO_2) as well as carboxylic acid end-groups, with deterioration of the mechanical properties [20–22].

This paper is an investigation on the behavior of EMBA resin to the UV radiations, using infrared (IR) and UV–vis spectroscopy, optical microscopy (OM) and weight loss determination.

2. Experimental

2.1. EMBA preparation

EMBA unsaturated polyesteric resin was obtained by a procedure described elsewhere [6], using maleic anhydride (MA) and commercial Dinox resin (Sintofarm-S.A., Bucharest, Romania), in presence of water, at 80 °C. Dinox resin, with epoxy equivalent of 0.84 and number-average molecular weight of 500, was obtained in reaction of bisphenol A with epichlorohydrin. The synthesized EMBA resin is characterized by a number-average molecular weight of 53,000, determined by gel permeation chromatography (GPC PL-END 950 apparatus) using PL gel 5 μm MIXED-D columns and *N*,*N*-dimethylformamide (DMF) as solvent. Calibration was performed by means of monodisperse polystyrene standard samples with narrow polydispersity (Polymer Laboratory GmbH, Darmstadt, Germany).

2.2. Irradiation and analysis

The film samples to be irradiated were prepared by casting from 10% DMF solution onto glass slides using a doctor-blading with a slit of 0.5 mm. The samples were dried under vacuum at 60 °C to complete remove of solvent. Samples with the same thickness (25 μm) were obtained by the regulation of the absorbance of the carbonyl stretching vibration to 1.0. The same surface area of the samples was used for irradiation experiments.

The EMBA film samples were irradiated in air, in an accelerated weathering rotative device equipped with a middle pressure mercury lamp HQE-40 type, heaving a polychrome emission spectrum in the field of 240–570 nm, with a hight intensity of 30 mW/cm^2. The more energetic radiations with $\lambda < 300$ nm, not presented in the natural light spectrum, were eliminated using a borosilicate glass filter. A water filter and a fan were used to prevent the thermal degradation of the sample during the photochemical treatment. The samples, as films, were mounted on a rotative device, which was positioned at a distance of 60 mm from the lamp. The temperature inside the irradiation chamber was kept around 40–45 °C. The mounted films were withdrawn from the device at different photo-oxidative times and analyzed using both IR and UV–vis spectroscopy, as well as OM technique.

The IR spectra of the studied samples were recorded with an M80 Specord spectrophotometer using KBr pellets and a nominal resolution of 2 cm^{-1}.

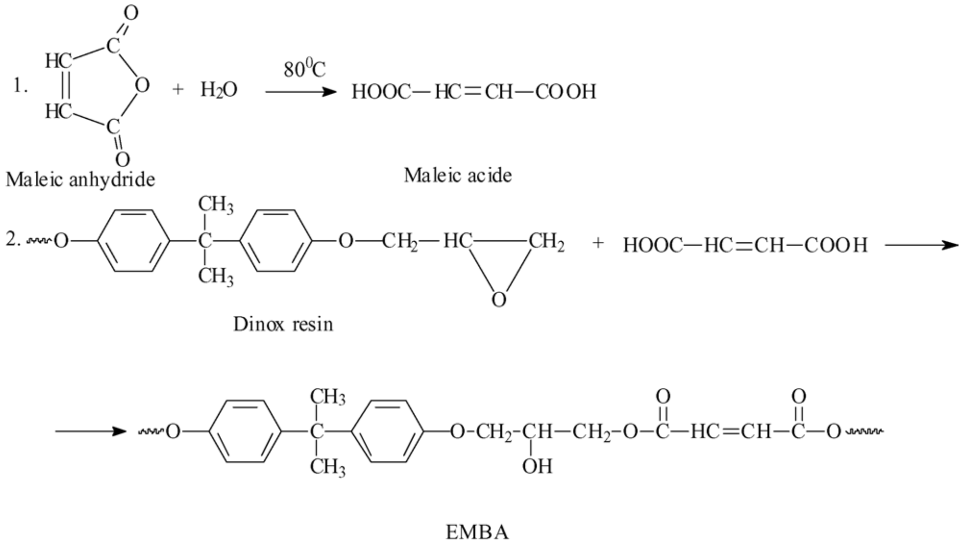
The OM micrographs were obtained by means of a MC5A (×300) optical microscope (IOR-Bucharest, Romania). Removing of the photodegradation products soluble in water was carried out by washing with distilled water.

The content of the gel fraction of UV irradiated EMBA sample was measured by extracting with DMF for 48 h in a Soxhlet apparatus. The weight of the nonsolubilized portion was measured after drying to constant weight.

The weight loss of the samples as against the irradiation time was estimated using the gravimetric method.

3. Results and discussion

The chemical reactions used for synthesis of EMBA resin are shown in Scheme 1.



Scheme 1. Synthesis of EMBA resin.

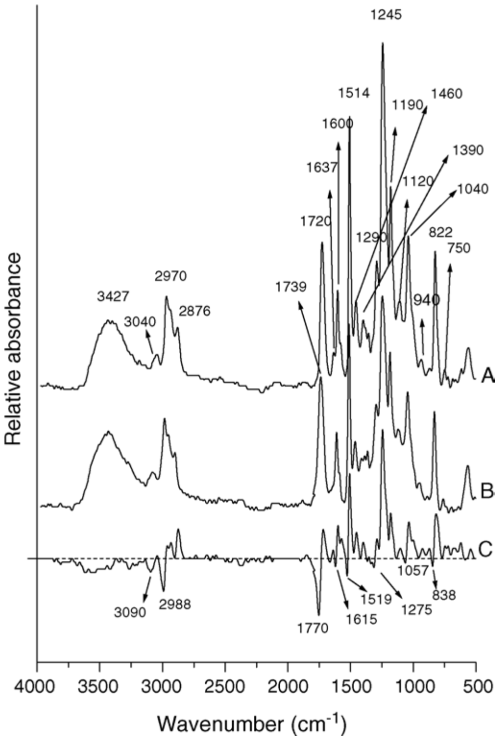


Fig. 1. IR spectrum of EMBA (A), after 20 h irradiation (B) and the difference A − B (C).

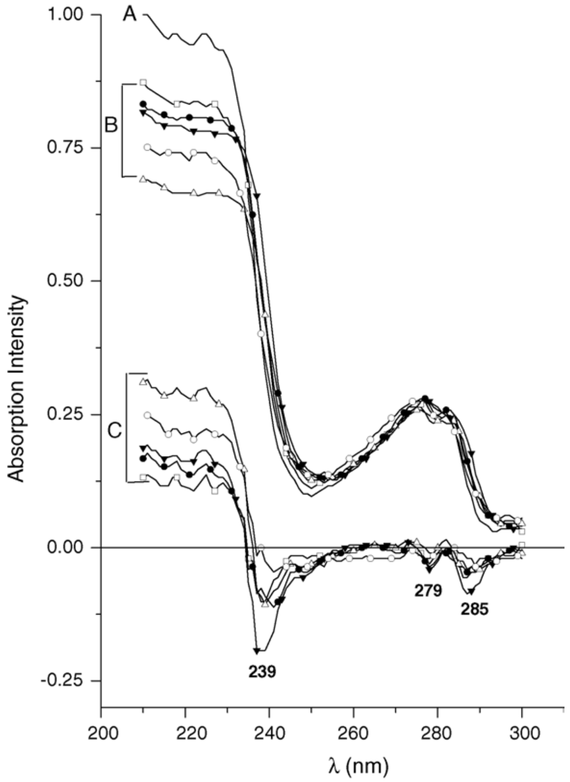


Fig. 3. UV–vis of EMBA (A), irradiated EMBA (B) for various exposure time: (□) 40 h, (●) 80 h, (△) 120 h, (▼) 140 h and (○) 180 h, and of the difference A − B (C).

As a consequence of the UV radiations many changes were observed in the IR spectrum of the EMBA sample. The IR spectra of nonexposed (A) and exposed (20 h) (B) EMBA sample films are shown in Fig. 1. The difference obtained by subtraction of the absorbances, which characterize both the spectra A and B, is also shown in Fig. 1 (IR spectrum C).

The assignment of the IR bands of the nonirradiated EMBA sample was carried out by means of the literature data regarding the IR analysis of the polyesteric resins [21–23]. The IR spectrum A shows a large band between 3100 and 3600 cm^{-1}, which is characteristic to the stretching vibration of OH group, and a band at 1720 cm^{-1} specific to the carbonyl stretching vibration in ester ($\nu_{C=O}$). The bands from 1290, 1245 and 1120 cm^{-1} characterize the symmetric and asymmetric stretching vibrations of C–O bond from EMBA esteric structure [15]. Both the stretching and the deformation characteristic vibrations at 1637, 940 and 750 cm^{-1} show the presence of the double bonds in EMBA structure. The bands from 3040, 1600, 1514 and 822 cm^{-1} are specific to the aromatic ring, while the band at 1190 cm^{-1} corresponds to the stretching vibration in ether bond [24]. The bands observed in the 2800–2990 cm^{-1} region characterize the valence vibration of CH_3–, –CH_2– and >CH– structures [25].

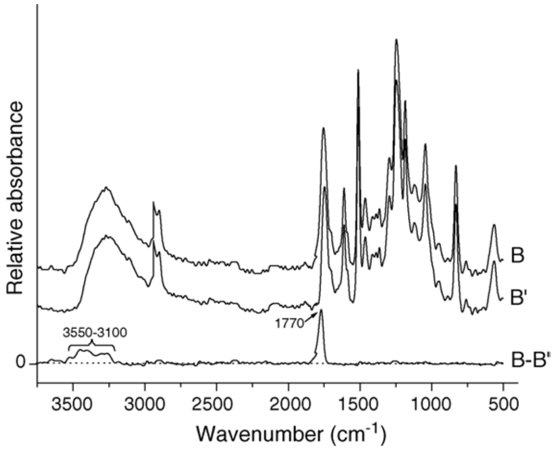
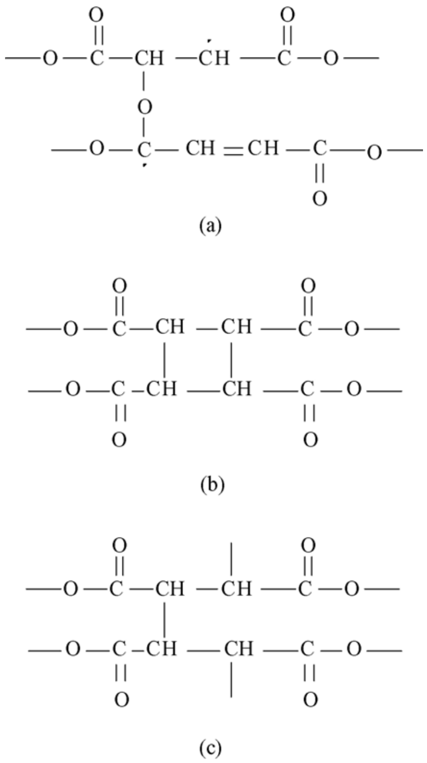


Fig. 2. The IR difference spectrum (B − B′) obtained as a difference between the IR spectrum of EMBA sample exposed to UV radiation for 20 h (B) and the IR spectrum of the same sample, which was heated at 180 °C, in N_2 (B′).

The IR spectrum B in Fig. 1 shows that the UV radiation induces modifications in the EMBA samples even after 20 h of exposure time. These modifications consist in some changes of the bands intensity. The effect of UV radiations on the EMBA samples is more clearly shown in the IR difference spectrum C, with negative and positive intensities. The negative absorbances reflect the new structures that were formed during the UV irradiation, while the positive absorbances mark those structures that were lost.

The difference spectrum C shows the diminution of the band intensities, which characterize both the unsaturated ester liaisons, together with the disappearance of the bands for the double bonds. Simultaneously, one can observe the displacement of the carbonyl stretching band from 1720 cm^{-1} to 1739 cm^{-1} after UV treatment. The disappearance of the double bond signals and displacement of the carbonyl absorbance to higher wavenumbers after UV irradiations are indications for the change of EMBA unsaturated polyester structures into cross-linked polyester structures.

The difference spectrum C is also characterized by the appearance of the new signals at 3090, 2988, 1770, 1615, 1519 and 836 cm^{-1} as well as in the 3100–3550 cm^{-1} region as a result of EMBA sample exposured to the UV irradiation. The bands in the 3100–3550 cm^{-1} region may be attributed to the presence of some associated hydroxyl groups and hydroperoxidic structures [26]. At 1770 cm^{-1} there is a band, which is characteristic for the peroxides [21]. The presence of both hydroperoxides and peroxides was confirmed by an experiment based on the thermal instability of such structures [27]. EMBA sample exposured 20 h to UV radiation was heated at 180 °C in N_2 for 1 h, under vacuum. The difference between the IR spectrum B before heating and IR spectrum B′ after heating (Fig. 2) is evidenced by a important decrease in intensity of the band in the 3100–3550 cm^{-1} region and the disappearance of the band at 1770 cm^{-1} (Fig. 2). This behavior is an indication of elimination of both hydroperoxides and peroxides [21,26].



Scheme 2. Some cross-linked structures possible to result on the UV irradiation of EMBA.

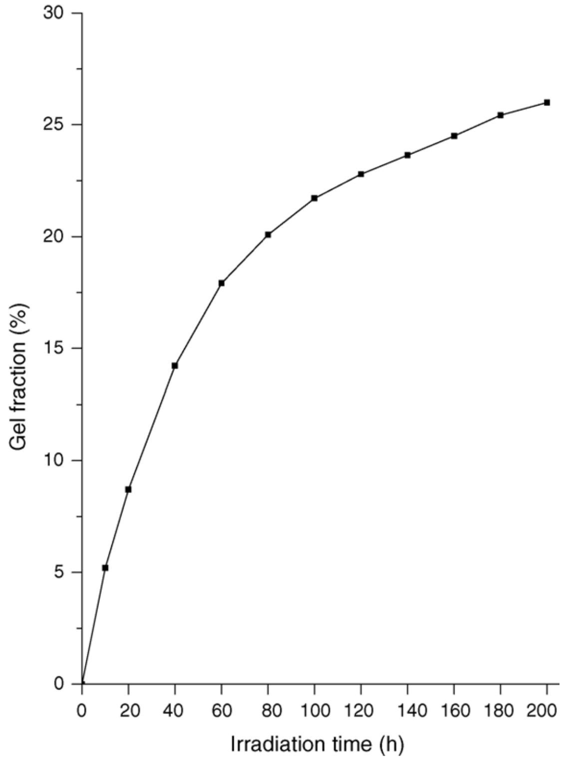


Fig. 4. Variation of the gel fraction against the irradiation time.

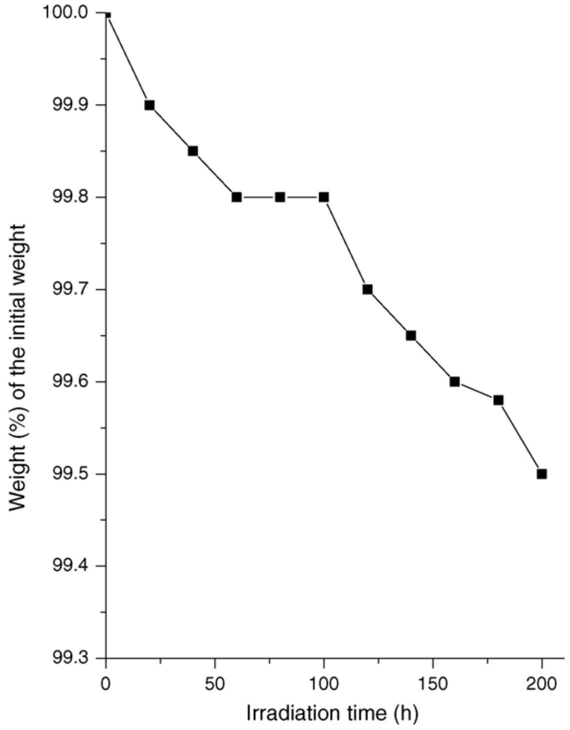


Fig. 5. Variation of the wt.% of the initial weight against the irradiation time.

The band at 2988 cm^{-1} in the IR spectrum C (Fig. 1) is specific to the C–H stretching vibrations from cross-linked structures [21]. The bands at 3090, 1615, 1519 and 836 cm^{-1} can be assigned to the aromatic structures [24], appeared as a result of UV treatment. These structures are linked by etheric liaisons (the band at 1275 cm^{-1}) with CH_3 groups ($–C_6H_4–O–CH_3$) [28].

The changes of the absorbances in the UV–vis spectra is shown in Fig. 3, where the UV–vis spectra of nonirradiated EMBA samples (A), irradiated samples (B) and the difference A − B (C) are presented.

It is evident from Fig. 3 that UV–vis spectrum of nonirradiated sample shows the strong absorption bands in the region 220 and 230 nm, which are specific to the unsaturated esteric structures, and a weak absorption band in the 274 and 285 nm attributed to the aromatic structures [29]. The bands in the 220 and 230 nm range continuous decrease with increase of the irradiation time. This is probably due to the destruction of unsaturated esteric structures under UV treatment. The build up of UV bands at 239, 279 and 285 can be assigned to the appearance of new aromatic eteric structures ($C_6H_4–O–CH_3$) that were formed as a result of the photodegradation process of EMBA sample. Fig. 3 shows also that there are not measurable absorptions at $\lambda \geq 300$ nm. This suggests that the photoinitioation of the degradation process of EMBA is due to the hydroperoxide photolysis [21].

To propose a mechanism of photodegradation of EMBA resin, we started first from the observation that the resin presents a very distinct conjugated system between the double bonds and the carbonyl groups, like other unsaturated

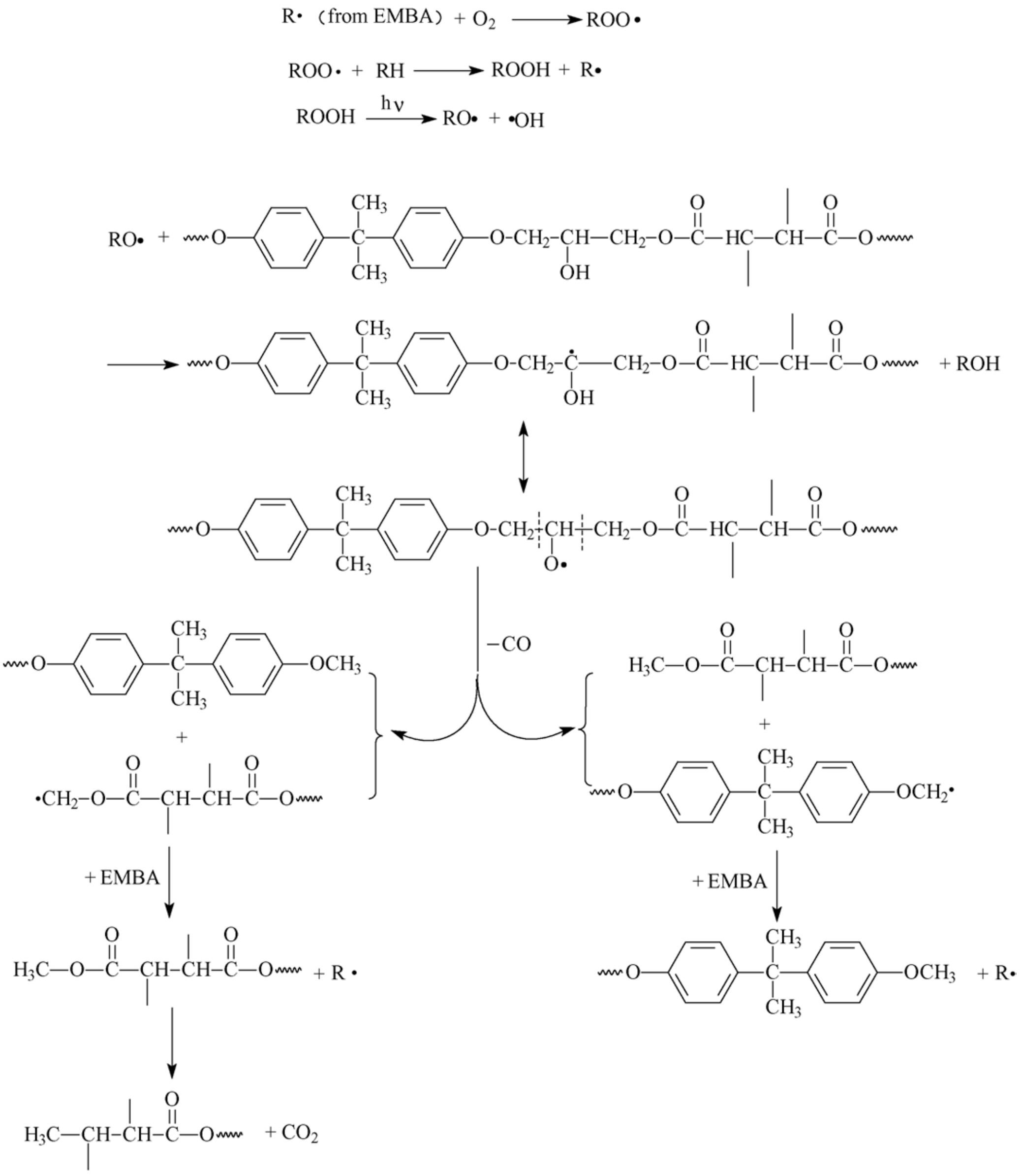
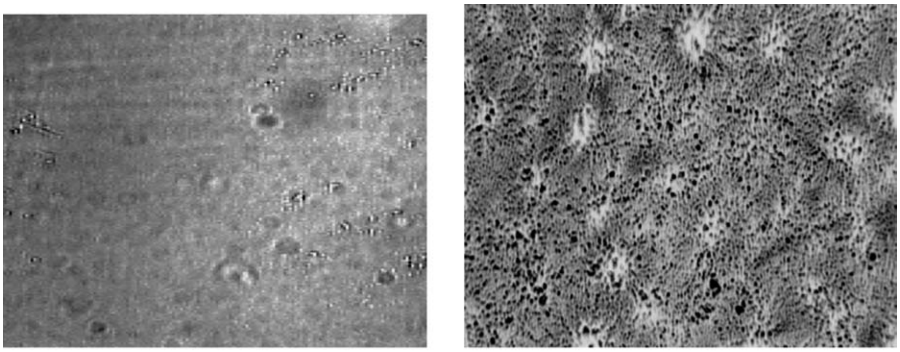
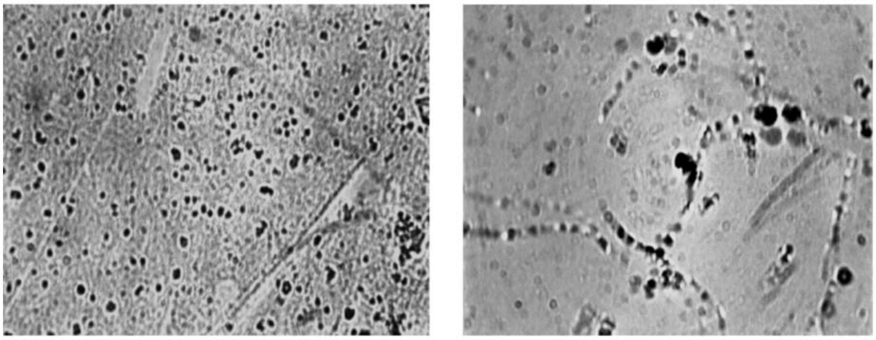


Fig. 6. The mechanism of photo-oxidative degradation of EMBA.



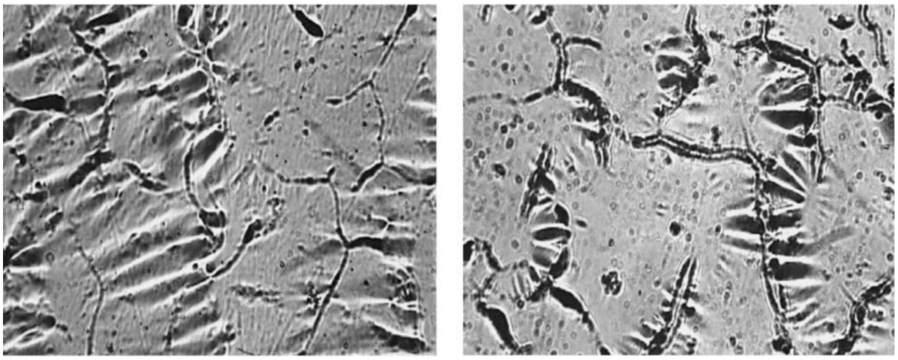
Unirradiatted EMBA

EMBA irradiated 40h



EMBA irradiated 80h

EMBA irradiated 120h

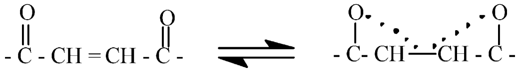


EMBA irradiated 160h

EMBA irradiated 200h

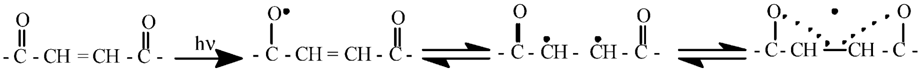
Fig. 7. OM micrographs of both nonirradiated and irradiated EMBA samples.

esteric resins [21] in the resonance form as:



$$-\overset{\overset{O}{\|}}{C}-CH=CH-\overset{\overset{O}{\|}}{C}- \rightleftharpoons -\overset{\overset{O\bullet}{|}}{C}-CH-CH-\overset{\overset{\bullet O}{|}}{C}-$$

In this case, the proposed mechanism presumes the disappearance of the double bonds under UV radiation with formation of the radicals.



$$-\overset{\overset{O}{\|}}{C}-CH=CH-\overset{\overset{O}{\|}}{C}- \xrightarrow{h\nu} -\overset{\overset{O\bullet}{|}}{C}-CH=CH-\overset{\overset{O}{\|}}{C}- \rightleftharpoons -\overset{\overset{O}{|}}{C}-\dot{C}H-\dot{C}H-\overset{\overset{O}{\|}}{C}- \rightleftharpoons -\overset{\overset{O\bullet}{|}}{C}-CH-CH-\overset{\overset{\bullet O}{|}}{C}-$$

As a result of the photodegradation process some rapid reactions between the radicals and the chain segments of the same or neighboring macromolecules take places forming cross-linked structures as those shown in Scheme 2.

A conclusive proof for this statement is the fact that the amount of the insoluble fraction increases with increase of the irradiation time (Fig. 4).

Some of the cross-linked ester structures may undergo a photolytic chain scission by the Norrish Type I reaction, with cleavage of the bond between the carbonyl group and adjacent α-carbon (CO and CO_2, elimination) [21,22]. As a result of the Norrish Type 1 reaction the decrease of the IR bands from 1720, 1290, 1245 and 1120 cm^{-1} takes place.

Although, there are many structural modifications of the EMBA samples due to UV radiations the content of volatile compounds evolved as a consequence of the photodegradation process is very low. The hydroperoxide formation by UV treatment of the EMBA sample makes as the absorption of oxygen to be one of the important factors, which leads to modifications of the sample weight. The change of the weight samples against the irradiations time is shown in Fig. 5.

As can be noted, the EMBA films lose only 0.5% of the initial weight after 200 h exposure time. This is an indication that the main chemical reactions occurred during the UV exposure of EMBA are photo-oxidative processes generated by hydroperoxide compounds.

The mechanism of photo-oxidative degradation of EMBA by hydroperoxide intermediates is suggested in Fig. 6.

Practically, quanta of light used in our experiments are sufficient in energy (95 kcal/mol) to split any C–C (83 kcal mol^{-1}) or C–O (86 kcal mol^{-1}) bonds from EMBA. The radicals ($R^\bullet$) may react with molecular oxygen, leading to the peroxy radicals. These radicals selectively abstract the hydrogen from a new molecule of EMBA and generate hydroperoxide groups. These groups may undergo unimolecular photolysis in both alkoxy and hydroxy radicals, which can easily abstract the hydrogen from the tertiary carbon of EMBA. The splitting of the macromolecular chains in small fragments, due to the β-cleavage of the C–C bonds, has as a result the formation of the ether aromatic structures. These structures were confirmed by means of IR and UV–vis spectra.

The optical micrographs carried out on the surface of the EMBA films, nonexposed and exposed to UV radiations, are shown in Fig. 7.

It can be noted that the surface of the nonexposed EMBA films is very smooth, with few small pinholes of 1–2 μm diameter. After 40 h exposure time EMBA films present holes of 2.0 up to 10.0 μm diameter, which were formed, probably, by removing of products with high volatility. In succession, after 160–200 h irradiation the formation of wrinkles and micro-cracks take place.

4. Conclusions

The UV radiation leads to important modifications of the EMBA samples, as was observed by IR, UV–vis and OM techniques.

It has been noted that the main photoreactions firstly involve the excitation of the double bonds in EMBA sample, with formation of radicals. The photo-oxidation of EMBA occurs by a free radical mechanism. In early stage of the photolysis of EMBA some cross-linked structures can be formed. These structures undergo secondary reactions with hydroperoxide formation.

Principally, the splitting of the EMBA chains, initiated by hydroperoxide compounds, leads to etheric aromatic structures, together with CO and CO_2 elimination. It has been remarked that the basic reaction occurred in photooxidative degradation of EMBA resin are similarly with that produced by thermal oxidative degradation [30].

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