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Effect of ultraviolet radiation on vinyl ester network based on bisphenol A

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Abstract

A vinyl ester resin (VER) based on bisphenol A (BA) was synthesized starting from a commercial epoxy resin (Ropoxid 501) and acrylic acid (AA). The synthesized VER was transformed into a vinyl ester network (VEN) in the presence of benzoyl peroxide. The behavior of VEN on UV radiation ($\lambda > 300$ nm), up to 200 h exposure time, was investigated using surface gloss measurements, differential scanning calorimetry (DSC), optical microscopy (OM), Fourier transform-infrared spectroscopy (FT-IR), UV–vis spectroscopy and weight loss. The UV radiation produces important modifications of VEN sample. Both the gloss index variation and OM micrographs show the presence of the roughnesses on the surface of VEN film. The decrease of the glass transition temperature with an increase of the irradiation time indicates the scission of the VEN chains under UV action. FT-IR and UV–vis spectroscopy evidence the presence of the photo-oxidative degradation products (hydroxyl and carbonyl groups, peroxides and hydroperoxides). The unstable hydroperoxides decompose by producing radicals that may attack the VEN chains. A possible mechanism of VEN photo-oxidative degradation was suggested.

Keywords: Vinyl ester resin; UV radiation; Photodegradation; Mechanism

1. Introduction

Vinyl ester resins (VERs) are the polymers obtained from the reaction between α,β-unsaturated acids and epoxy resins [1]. A VER has the double bonds as the end groups, which are derived from the acid structure. The presence of the reactive double bonds in the VER structure is a way to obtain the cross-linked networks by initiation with the free radicals. Due to their high strength, high durability, thermal stability and extremely high corrosion resistance, VERs are the polymer matrices used for manufacturing of high-performance composites intended to marine, aerospace, transportation, building constructions and biomedical applications [2–6].

The durability of VER-based composites in outdoor environment is restricted by the damage of the polymer matrix in the presence of some destructive factors, such as: the moisture, acid rain and UV. UV radiation is potentially the most damaging to VER-based materials. Under the action of UV from the solar spectrum (4–6%) the polymers undergo photolytic and/or photo-oxidative reactions with negative effects that range from the discoloration, yellowing or surface gloss loss through the failure of the mechanical properties [7–9].

After our knowledge, very few data were published on the behavior of VERs to the UV radiation [9,10]. In their papers the authors concluded that VER matrix composites, in the presence of the UV light undergo severe degradations with changes in the surface chemistry, morphology and bulk matrix. The aim of this study was to investigate the photochemical processes occurred in a vinyl ester network (VEN) based on bisphenol A (BA) during irradiation with near ultraviolet radiations ($\lambda > 300$ nm).

2. Experimental

2.1. VEN preparation

First, a VER based on bisphenol A (VER-BA) was obtained by the procedure described elsewhere [11–13]. The synthesis was carried out using commercial Ropoxid 501 resin (Policolor SA Bucharest, Romania) and acrylic acid (AA), in the presence of benzyltributylammonium chloride (BTAC), as catalyst. Ropoxid 501 resin, with epoxy equivalent value 0.525 equiv. 100 g^{-1} and number-average molecular weight ($\bar{M}_n$) of 381 g mol^{-1}, was obtained in reaction of BA with epichlorohydrin (EPI). The synthesized VER-BA resin, solu-

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ble in dimethylformamide (DMF), is characterized by $\bar{M}_n = 525\,\mathrm{g\,mol^{-1}}$ and melting point 53 °C. The VER-BA films were obtained from DMF solutions. The films were dried under vacuum at 60 °C and cross-linked in the presence of benzoyl peroxide (BP) at 100 °C, when a tridimensional, insoluble and infusible VEN was obtained.

2.2. Irradiation and analysis

Samples with the same thickness (25 μm) were obtained by adjustment of the absorbance of the carbonyl stretching vibration to 1.0.

The VEN film samples with the same surface area were irradiated in air, in an accelerated weathering rotative device, equipped with a fluorescent lamp UVA-351 type. The lamp had a polychrome emission spectrum in the field of 300–540 nm, with the peak wavelength at 365 nm, and a light intensity of $30\,\mathrm{mW\,cm^{-2}}$. The more energetic radiations ($\lambda < 300$ nm), not found in the sunlight spectrum at earth's surface, were eliminated using a borosilicate glass filter. A water filter and a fan were used to prevent the thermal degradation of the samples during the photochemical treatment. The film samples 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 times and analyzed using Fourier transform-infrared spectroscopy (FT-IR), UV–vis spectroscopy, optical microscopy (OM), differential scanning calorimetry (DSC), surface gloss and weight loss measurements.

The FT-IR spectra were recorded with a FT-IR Spectrometer Bruker Vertex 70 Spectrophotometer. Spectra were recorded at a resolution of $4\,\mathrm{cm^{-1}}$ and 128 scans. The peak surface was used to evaluate the IR intensity, which is expressed in absorbance.

The UV–vis absorption spectra were obtained using an UV–vis M-42 type apparatus.

The concentration of the hydroperoxides was measured by an iodometric method [14,15], using a Cole Palmer 1100 RS Spectrophotometer.

The OM micrographs were obtained by means of a MC5A (300×) optical microscope (IOR-Bucharest, Romania).

A Power-Compensation PYRIS Diamond DSC apparatus (Perkin-Elmer) was used to determine the glass transition temperature (T_g) of the VEN resins. Samples (8–10 mg) were scanned under nitrogen at $10\,°\mathrm{C\,min^{-1}}$ heating rate. The T_g values were evaluated using the second scan to assure identical thermal histories.

The modification of the sample gloss surface during irradiation was monitored by means of the Gloss Chacker IG-320 apparatus (Horiba Ltd., Japan). The gloss value was determined comparing the intensity of the sample luminous reflection with the value registered for a standard surface (polished black glass).

The variation of the sample weight versus the irradiation time was estimated by a gravimetric method, using an ADAM PW-254 model analytical balance. The averages of four measurements, with a maximum deviation ±2%, were taken into consideration.

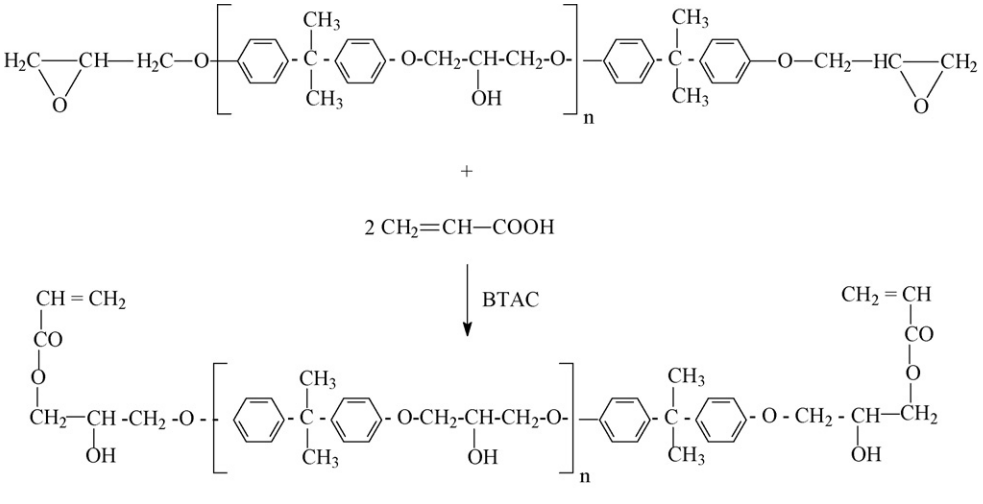
3. Results and discussion

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

The cross-linking process of VER in the presence of BP was monitored by means of FT-IR spectroscopy. Fig. 1 shows the FT-IR spectra recorded for both VER (A) and VEN (B) samples, while Table 1 lists the peaks assignment in the VER FT-IR spectrum.

The assignment of the IR bands was carried out by means of the literature data regarding the IR analysis of the polyester resins [16–18].

As a result of the cross-linking reaction, the vibrations, which are characteristic to the double bond (1635 and $940\,\mathrm{cm^{-1}}$; Fig. 1, spectrum A), disappeared (Fig. 1, spectrum B), while the vibration at $1382\,\mathrm{cm^{-1}}$ diminished. The FT-IR spectrum B in Fig. 1 shows an enlargement of the peak at $1488\,\mathrm{cm^{-1}}$, which is characteristic to the deformation of $-CH_2-$ group. The peak at $1712\,\mathrm{cm^{-1}}$ in the spectrum A, (valence vibration of C=O



Scheme 1. Synthesis of VER resin.

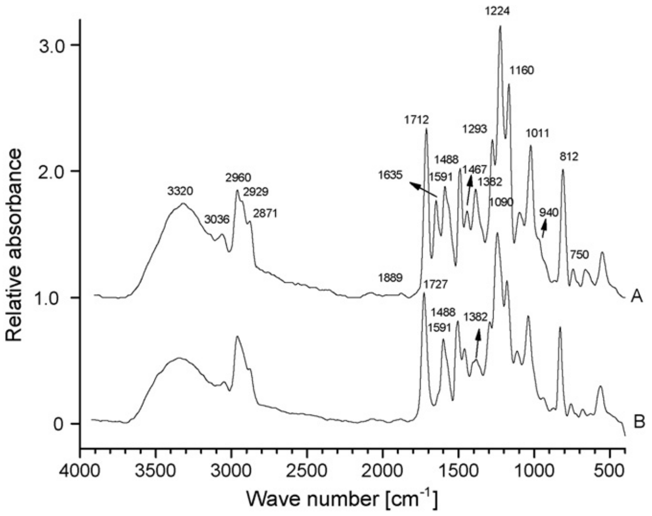


Fig. 1. FT-IR spectra of VER (A) and VEN (B) samples.

Table 1
IR characteristic bands of VER

Wavenumber (cm^{-1})	Main assignment
3320	νOH associated
3036	νCH of the aromatic ring
2960/2929/2871	νCH/νCH$_2$/νCH$_3$
1889	γCH aromatic ring
1712	νC=O
1635	νC=C double bond
1591	νC=C aromatic ring
1488	δCH$_2$ or/and δCH$_3$
1467	Aromatic ring stretch
1382	δCH$_2$ or/and δCH of the double bond
1293	νC—O
1224	νC—O—C
1160	νC—CO—O
1090	δCH aromatic ring
940	δCH double bond
812	Polyhydroxyether backbone
750	γCH aromatic ring

group), was replaced by the peak at 1727 cm^{-1} in the spectrum B. The FT-IR spectra showed that the synthesized VER was cross-linked by means of the end double bonds leading to a new synthetic product with a network structure (VEN) (Scheme 2).

As a consequence of the UV radiation many changes were noticed in the VEN sample. Fig. 2 shows that the gloss of the VEN film surface gradually decreases from 99.5 up to 32.7, within 200 h exposure time. Apparently, the initial gloss loss occurred after 40 h irradiation time. The decrease of the gloss value with the irradiation time is based on the relationship between the surface roughness and the reflection. The rough surface is less glossy, and when a polymer is broken up its surface gloss is lost progressively [19,20].

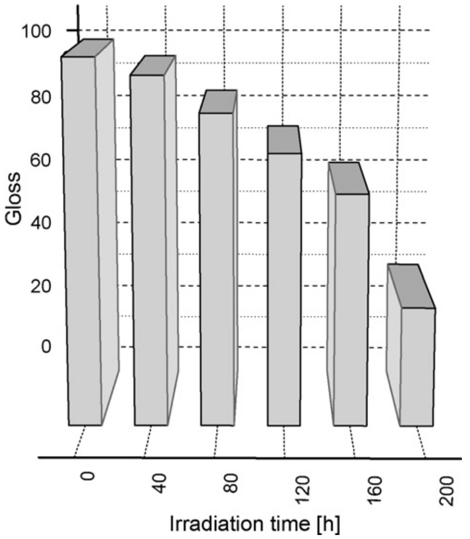
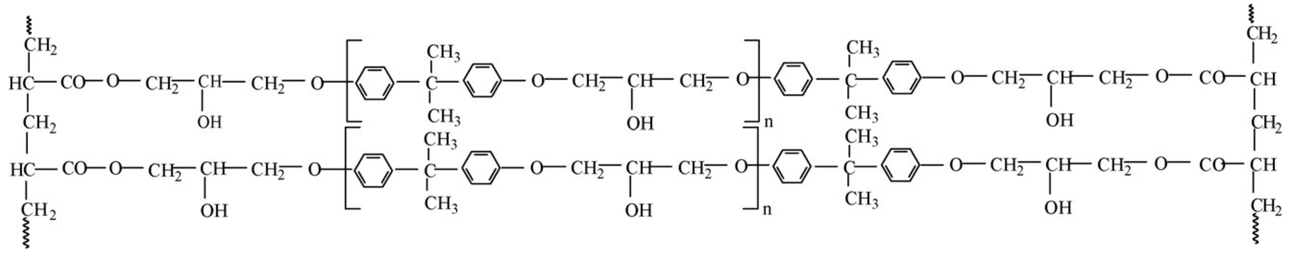


Fig. 2. Variation of the surface gloss of VEN against the irradiation time.

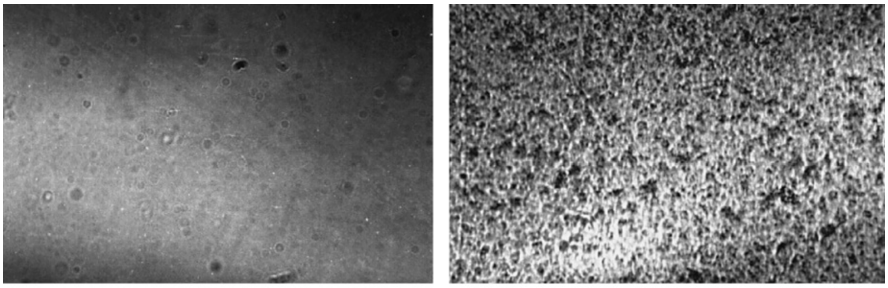
The roughness increase on the surface of VEN sample after 200 h irradiation time is evidenced by OM technique. The VEN non-irradiated sample shows a smooth surface penetrated by some pinholes up to 10 μm maximum diameters (Fig. 3). After 200 h irradiation times the surface becomes very rugous, being characterized by numerous large pinholes and micro-cracks. The modification of the VEN surface morphology confirms the destructive effect due to the UV radiation.

The UV radiation has an important influence on the sample weight. The variation of the sample weight against the exposure time in shown in Fig. 4. A gentle increase of the VEN sample mass (0.2–0.5%) takes place in the first 10 h irradiation, due to the participation of the oxygen from air to generate the hydroperoxides [13]. The presence and the accumulation of hydroperoxides on the surface of VEN films (Table 2), their instability and fragmentation led to products with the low molecular weight and the high volatility. The loss up to 9% from the initial sample weight after 200 h exposure time is an indication for VEN photodegradation, with elimination of volatile compounds (CO, CO$_2$, H$_2$O, etc.).

Table 2 shows that the content of hydroperoxides in the VEN sample increases with an increase of the irradi-



Scheme 2. Structure of VEN resin.



VEN non-irradiated sample (x300)

VEN sample irradiated 200 h (x300)

Fig. 3. Optical micrographs of VEN sample.

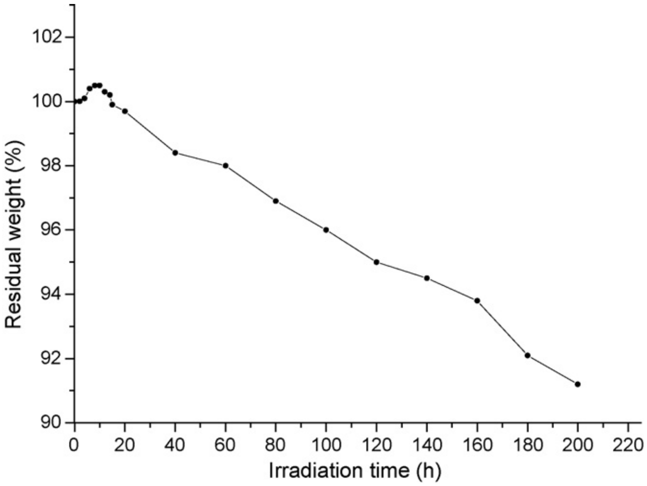


Fig. 4. Residual weight on UV irradiation of VEN sample.

ation time up to around 400 min, when a critical value of 17.5×10^{-5} mol (OOH)/g polymers is enough for the photodegradation.

The change of T_g of VEN sample during UV irradiation was examined using DSC technique. Table 3 shows that the T_g value of the VEN sample decreases with an increase of the irradiation time. This behavior means a diminution of the molecular weight of the polymers due to UV irradiation [21]. The decrease of the T_g values with irradiation time is accompanied by an increase of the glass transition width from 7 °C for non-irradiated sample up to 11 °C for the sample irradiated 200 h. This behavior evidences the storage of the photodegradation products in the mass of the sample during UV exposure.

Table 2
Variation of the hydroperoxide concentration during the exposure of VEN sample to UV radiation

Irradiation time (min)	Hydroperoxides content ($\times 10^{-5}$ mol (—OOH)/g polymer)
10	7.0
50	9.4
100	12.6
150	14.3
200	15.2
250	15.8
300	16.3
350	16.9
400	17.5
450	17.9
500	17.7
550	17.5
600	17.5

Table 3
T_g and transition width of the VEN sample versus the irradiation time

Irradiation time (h)	T_g (°C)	Transition width (°C)
0	96	7
80	90	8
160	88	10
200	85	11

FT-IR spectroscopy is a sensitive and reliable technique, which allows to quantify the chemical changes in the polymeric materials during UV irradiation [22–24]. UV with $\lambda > 300$ nm leads to significant changes in the FT-IR spectrum of VEN sample. The FT-IR spectra of both non-irradiated (spectrum 1) and 20 h irradiated VEN sample films (spectrum 2) are shown in Fig. 5. The spectrum difference obtained by subtraction of the absorbances of the spectrum (2) from the spectrum (1) is also shown in Fig. 5 (spectrum 3).

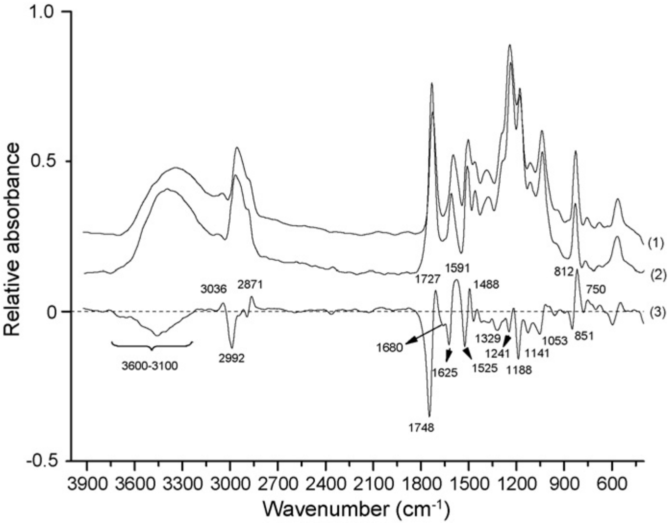


Fig. 5. FT-IR spectra of VEN: (1) non-irradiated; (2) irradiated 20 h; (3) (1) and (2) difference.

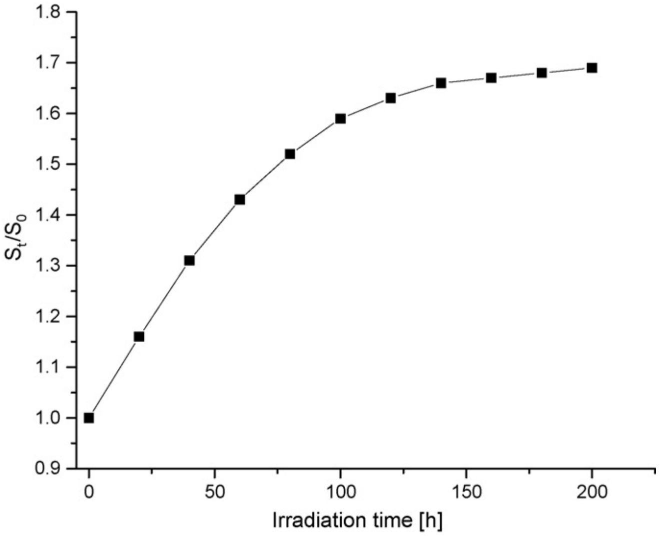


Fig. 6. Change of —OH group content against the irradiation time.

The change both of the hydroxyl and of the carbonyl absorption signals during UV irradiation, as the peaks area between 3700 and 3100 cm^{-1} and 1850 and 1650 cm^{-1}, respectively, was evaluated as a measure of the photodegradation rate. The ratio of the peak area of VEN sample at different exposure time (S) against the surface of the peak area of the non-irradiated sample (S_0) was calculated.

The spectrum difference (3) shows some positive absorbances at 3036, 2871, 1727, 1591, 1488 and 812 cm^{-1}, which can be assigned to the partial decomposition of the aromatic rings of the saturated ester functions, as well as to the polyhydroxy ether backbone from VEN structure. The negative absorbances in the same spectrum (3) correspond to the new structures that were formed during UV irradiation. The enlargement of OH groups signal at 3320 cm^{-1} is an indication of the photodegradative reactions occurred in VEN structure through an oxidative mechanism [25].

Taking into consideration the variation of OH signal with the irradiation time (Fig. 6), the plot of absorbance at 1591 cm^{-1} for the aromatic ring against the exposure time (Fig. 7) and the apart behavior of the absorbance at 1727 cm^{-1}, which is characteristic to the carbonyl group (Fig. 8), a kinetics of the VEN photodegradation was established.

The curve in Fig. 6 shows that the OH groups content increases faster in the first 80 h irradiation time, then slows down and tends to achieve a plateau.

The absorbance at 1591 cm^{-1}, which is characteristic to the aromatic ring, decreases after a straight line against the exposure time (Fig. 7). This means a photo-oxidation of the aromatic ring, which leads to some unsaturated compounds with carbonyl groups in their structures. Such structures are confirmed by the new signal at 1680 cm^{-1} (Fig. 5). The change of the absorbance in the carbonyl region must be carefully interpreted, because the FT-IR spectrum of VEN shows two opposite tendencies, namely: (1) the decrease of the absorbance from 1727 cm^{-1} with an increase of the irradiation time, and (2) its shift to higher wave numbers (up to 1800 cm^{-1}) (Fig. 8).

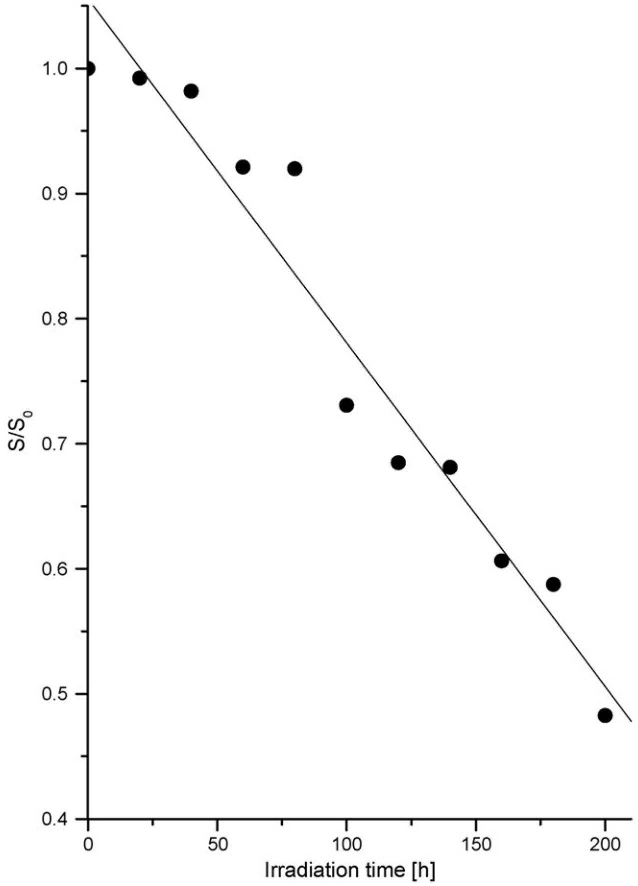


Fig. 7. Change of the aromatic ring absorbance against the irradiation time.

The decrease of the absorbance from 1727 cm^{-1} is due to the photolysis of the saturated ester function. The variation of the carbonyl absorbance versus the irradiation time is shown in Fig. 9.

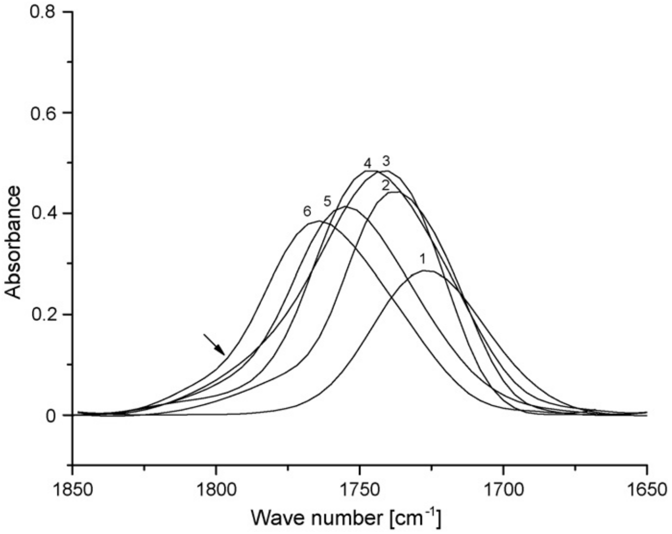


Fig. 8. Evolution of the FT-IR spectra in the carbonyl region (1850–1650 cm^{-1}) with the irradiation time: (1) VEN, non-irradiated sample, (2) irradiated 20 h, (3) irradiated 40 h, (4) irradiated 80 h, (5) irradiated 100 h, and (6) irradiated 200 h.

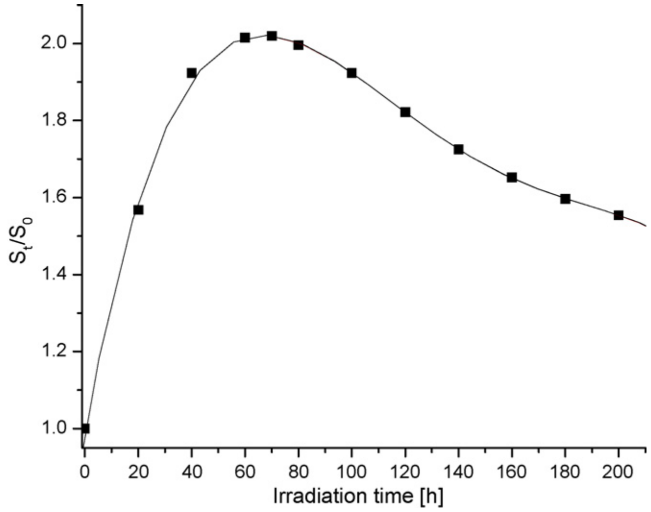


Fig. 9. Normalized absorption of the carbonyl band vs. the irradiation time.

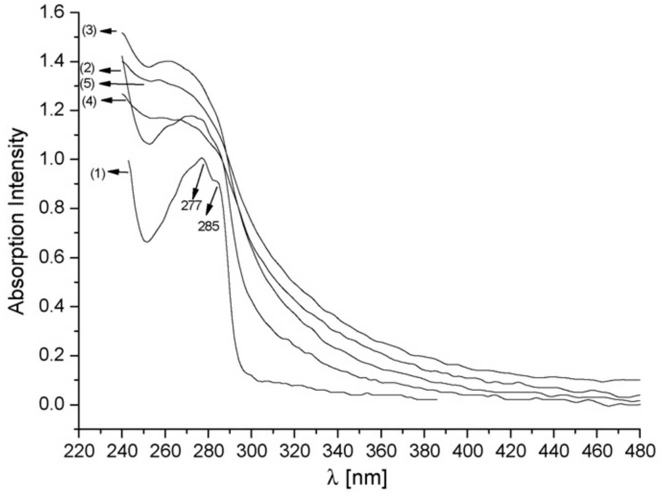


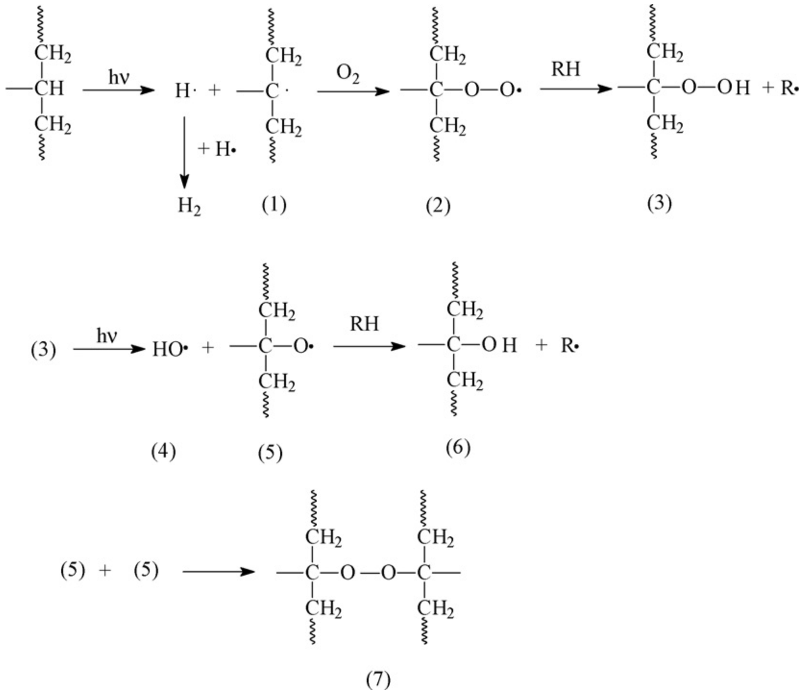
Fig. 10. Modification of UV–vis spectra of VEN sample with the irradiation time: (1) non-irradiated sample, (2) irradiatied 20 h, (3) irradiated 40 h, (4) irradiated 60 h, and (5) irradiated 80 h.

As can be noted, the carbonyl absorbance value increases with a high rate in the first 70 h UV exposure time. This behavior can be due to the presence of some photosensitive groups with peroxide structures. Both the peroxides and the compounds with hydroxyl groups in their structures can result by photodecomposition of the hydroperoxides, which are highly unstable and undergo homolitic reactions (Scheme 3) [14,18,26,27].

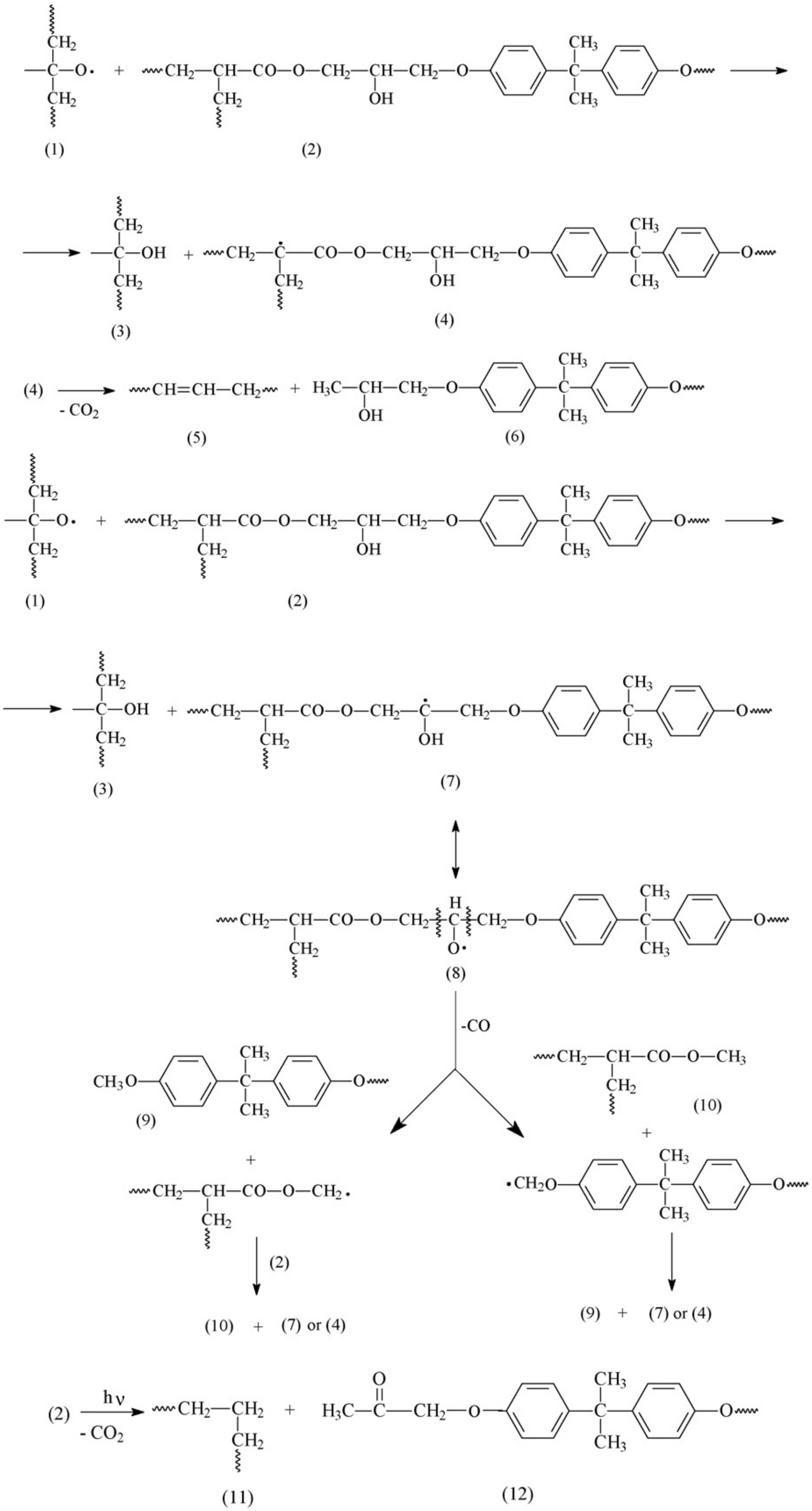
The type 1 Norrish reactions, accompanied by the hydrogen transfer, could explain both the partial decomposition of the saturated ester structures and the appearance of the new products bearing –CH=CH– double bonds (1625 cm^{-1}), carbonyl groups (1748 cm^{-1}), aromatic ethers (1241 cm^{-1}) and $–CH_2–$ groups (2962 and 2872 cm^{-1}) [8,13,28,29]. The VEN macromolecular chains split in β position of the saturated ester structure, with elimination both of CO and CO_2 compounds. Taking into consideration the hydroperoxide decomposition with the free radicals formation (Scheme 3) and the FT-IR data, a possible photo-oxidative degradation mechanism of VEN sample was suggested (Scheme 4).

The UV radiation effect on the VEN sample was studied and by UV–vis spectroscopy. Fig. 10 shows the UV–vis spectra of VEN sample, which were obtained at various irradiation times.

The UV–vis spectrum of VEN non-irradiated sample shows a strong absorption at 277 nm and a shoulder at 284 nm, attributed to the aromatic structures [13,28–31]. The bands enlarge and increase with the irradiation time, due to the appearance of the new aromatic ethers, such as the product labeled (9) in Scheme 4.



Scheme 3. Compounds with hydroxyl groups, hydroperoxides and peroxide structures resulted during irradiation of VEN resin.



Scheme 4. The photo-oxidative degradation mechanism of VEN resin.

The development of some absorbances at longer wavelength (300–400 nm), together with the increase of the irradiation time, could be an indication for the formation of new chromofores with conjugated carbonyl groups [14,32]. The presence of such structures can explain the photoyellowing of VEN sample during UV irradiation.

4. Conclusions

The VEN based on VER-BA resin was prepared in the presence of BP and was exposed to UV with $\lambda > 300$ nm. The UV radiation led to important modifications of VEN sample, as was observed both by the weight loss and by the surface gloss measurements, as well as by DSC, FT-IR and UV–vis techniques.

The VEN surface gloss decreases progressively versus the irradiation time. In the presence of the oxygen from air, the appearance of the hydroperoxides takes place in the first 10 h exposure time. As a result of the hydroperoxides instability, their fragmentation leads to products with low molecular weight and high volatility. The splitting of the VEN chain in the presence of hydroperoxides leads to saturated ester functions and polyhydroxy ether structures, together with CO and CO_2 elimination.

The oxidative mechanism, photo-oxidation and photodegradation kinetics of the VEN samples were analysed taking into consideration the behavior both of the hydroxyl and the carbonyl FT-IR absorption bands during irradiation.

The appearance of the chromofore products with conjugated structures led to the light absorption at longer wavelengths. This could explain the photoyellowing of the samples.

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