REVIEW PAPER

The degradation of thin poly(methyl methacrylate) films subjected to different destructive treatments

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Abstract

A comparative study of the degradation of poly(methyl methacrylate) (PMMA) films deposited on metal mirrors as a result of heat treatment or irradiation with various UV or γ radiation is presented. The main degradation processes of PMMA during degradation are the random homolytic breakdown of carbon–carbon bonds in the polymer main chain and the photolysis of the lateral methyl groups and lateral esters to form free radicals. All observations on the reflection–absorption spectra are in agreement with the mechanism of PMMA film degradation, subjected to various types of destructive degradation: thermal heating, UV irradiation, or γ irradiation. Unlike other approaches, this one used the reflection–absorption spectra of PMMA thin films deposited on metal mirrors.

Introduction

A lot of structural transformations of poly(methyl methacrylate) (PMMA) thin films occur as a result of heat treatment or irradiation with various UV or γ radiation, such as:

- random homolytic cleavage of main-chain carbon–carbon bonds in the main chain of the polymer;
- photolysis of the methyl side groups and ester side groups with formation of radicals: acethyloxy ($\cdot COOCH_3$), methoxy ($\cdot OCH_3$), formyl ($\cdot CHO$) and methyl ($\cdot CH_3$);
- formation of double bonds in the polymer chain;
- formation of methyl formate, methyl methacrylate, methanol, carbon monoxide and carbon dioxide;
- formation of ketone polymers or polymers, containing alcoholic hydroxyl groups or carbonyl [1–11].

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The structural transformations of PMMA are highlighted by changing the appearance of its infrared spectra. Intensity changes, broadening and shifts of absorption bands occur. Increases or decreases of absorption bands intensity occur due to photolysis of methyl or ester side groups followed by degradation processes and transformation of radical formed. The shift of the absorption bands to lower or higher frequencies occur as a result of the weakening respectively of the intensification of the bonds between atoms during the photolysis of the polymer and of the appearance of the degradation products.

The infrared reflection absorption spectroscopy (IRRAS) is one of the most common and straightforward external reflection techniques. This technique, of infrared reflection–absorption spectroscopy, was first described by Francis and Ellison [12] and further developed by Greenler [13]. The technique is very often used for grazing incident reflection (GIR) and for very thin surface films. The radiation used is the one parallel polarized to the incident plane.

There are many papers in the literature that use the FTIRRA (infrared reflection–absorption with Fourier transform) technique of external reflection at grazing incidence angle for study of monolayers and very thin films (of the order of tens or hundreds of nanometers) [12–17]. Not for micron thick films. Most papers use the FTIRRA technique with many scans.

For thick films, the specular external reflection was used, and the Kramers–Kronig transform of the recorded reflection spectrum allows us to obtain the spectrum of the refractive index and the spectrum of the absorption index.

The originality of this paper consists in the use of IR reflection–absorption spectroscopy in the study of PMMA films with thicknesses of the order of microns without using multiple scan and Fourier transform of spectra. We used a much simpler reflection–absorption technique, which records the IR spectrum following a single external reflection, at small angles of incidence.

In the case of reflection on polymer thin films (with thicknesses of less than 20 μm) deposited on metal mirrors, as in Fig. 1, the reflected radiation contains two components: one reflected by the air-film (of intensity I_r) and one reflected on the metal-film interface (of intensity I_t), after having crossed the polymer film twice.

For thin films with micrometers thickness deposited on metal mirror, the reflection spectrum becomes a transmission spectrum of the thin film with twice the effective thickness of the actual one when the incident angle φ_0 is small. The IR radiation is usually incident on the sample at small incidence angles of $(10–50^0)$. The film should be on a reflective support [18].

The values of the refractive indices for many polymers are less than 1.6. As a result, the reflectance at the air-film interface, for the 20^0 incidence angle, is 0.04 (4%) [10]. This means that only 4% of the intensity of the incident radiation is reflected and the remaining 96% is refracted in the polymer film. Then the radiation is reflected on the polymer-metal interface. The reflecting surface is a steel mirror having in middle-IR the refractive index n = 3–9 and absorption index k = 9–58 [19]. The reflectance at the polymer-steel interface is a medium value of 0.894. So 89.4% of the intensity of the incident radiation, after reflection on the metal mirror, passes through the polymer film again. At the polymer-air
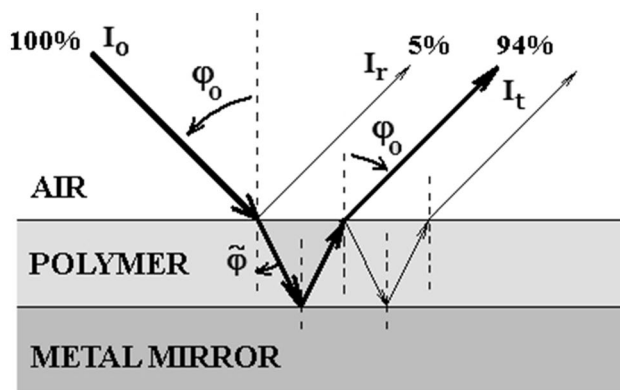
Fig. 1 Specular reflection of radiation on thin polymer film deposited on the metal

interface the radiation is refracted. Here again 0.04% of the radiation is reflected inside the polymer film. Thus, the radiation that is reflected from inside the polymer on the metal mirror has an intensity of 85.8% of the intensity of the incident radiation. The intensity of the radiation reflected at the polymer-metal interface that crosses the polymer film twice is thus about 85.8% of the intensity of the incident beam, being almost 21.5 times more intense than the beam reflected directly at the air-polymer interface.

Under these conditions, the infrared reflection–absorption (IRRA) spectrum is dominated by absorption since specular reflection from the air-film interface is only 4–10%, as shown by Fig. 1. For this reason the IRRA spectrum is very similar to the infrared transmission spectrum. The obtained spectrum is a reflection–absorption (or transflection) spectrum. It is similar in terms of quality of the transmission spectrum of the polymer film [20].

Unlike other approaches, this one used the reflection–absorption spectra of PMMA thin films deposited on metal mirrors.

The aim of the paper is to show how well the changes of the appearance of the IR spectra and of the PMMA structure are highlighted at various types of degrading actions on the polymer by using reflection–absorption IR spectroscopy at near-normal incidence. In the case of reflection–absorption spectroscopy (RAS) at near-normal incidence, the IR beam is directed to the sample within the angular range of $10–50^0$ [18].

In our paper, we qualitatively highlighted the changes in the aspect of the IRRA spectrum of PMMA films subjected to the action of three destructive processes: light heating (less destructive) at temperatures close to Tg of PMMA, UV irradiation, and gamma-irradiation.

The influence of temperature on changes in the structure of PMMA and thus on the appearance of the IR spectrum was investigated in many papers [1–6]. The mechanism of PMMA photodegradation and changes in the polymer spectra during UV irradiation were analyzed in many papers [7–10, 21, 22]. The influence of gamma rays on the properties of PMMA and composites was investigated in many papers [23–29].

Experimental

The poly(methyl methacrylate) (PMMA) thin films on steel substrates were examined. The OLC-35 steel surface (about 6.7 cm^2) used as substrate for the polymer film was obtained by grinding and polishing in order to obtain a mirror of good quality.

Thin films of PMMA were obtained by depositing a solution of polymer dissolved in benzene. We considered benzene as a good solvent for dissolving the polymer [30].

The concentrations of the solutions used were 0.5–4 g/L. Quantities of solutions of such a concentration were deposited on the horizontal surface of the metal mirror, in order to obtain films with thicknesses of the order of microns. The sample on which the polymer film was deposited was coated with a Griffin beaker for slow evaporation of the solvent. In this way, superficial films of relatively constant thickness were obtained. Low concentrations of the polymer in the solvent allowed us to obtain thin films with thickness less than 10 μm, without interference fringes as a result of non-uniform thickness.

Next, the samples were dried for 15 min at 80 ^{0}C and pressure of 12 Pa to remove the solvent residue. Commercial (Montedison, Italy) atactic poly(methyl methacrylate) granules ($M_w \sim 97$ kg/mol by GPC, $M_n \sim 46$ kg/mol, $T_g = 105$ ^{0}C, $T_m = 150$ ^{0}C) were used, without any further purification.

The IR reflection-absorption spectrum was recorded at 20^0 incidence angle after evaporation of the solvent, before heat treatment or irradiation of the polymer film. The IR reflection–absorption spectra were recorded within the spectral range of 500-4000 cm^{-1} with the Carl Zeiss Jena UR-20 spectrophotometer with specular reflectance accessory. The PMMA film deposited on the steel mirror was subsequently subjected to a heat treatment or irradiated with UV or γ radiation. The PMMA spectra were then recorded again after the treatments applied.

The heat treatment of the PMMA film deposited on the metal mirror was performed for 2 h at 120 ^{0}C in order to remove the solvent used.

A low-pressure mercury vapor lamp emitting radiation of 254 nm wavelength was used for UV irradiation of the samples (at an irradiance of 800 W/m^2). Irradiation of the polymer film with UV radiation was performed for various irradiation times between 2 h and 17.5 h.

The poly(methyl methacrylate) films on metal mirror were irradiated at room temperature in cobalt-60–based gamma chamber (2490 Ci, Gamma chamber) with 2 kGy h^{-1} dose rate.

The thickness of the surface polymer films that showed interference fringes in the reflection–absorption spectrum was obtained by interpreting the interference fringes [31]. The least-square fitting of PMMA R-A spectra using simple model dielectric functions, such as Drude-Lorenz oscillators, also called the dispersion analysis, was used in order to obtain the thickness of the polymer films without interference fringes [32, 33].

Results and discussion

The IR reflection–absorption spectrum of the thin PMMA film deposited on the steel mirror recorded at 20^0 incidence angle is shown in Fig. 2. The spectral range 500-4000 cm^{-1} (which contains the main absorption bands of the PMMA film) was recorded. For incidence angles less than 50º the reflectance R and transmittance T values depend slightly on the angle of incidence as shown in Fig. 1 [18, 34].
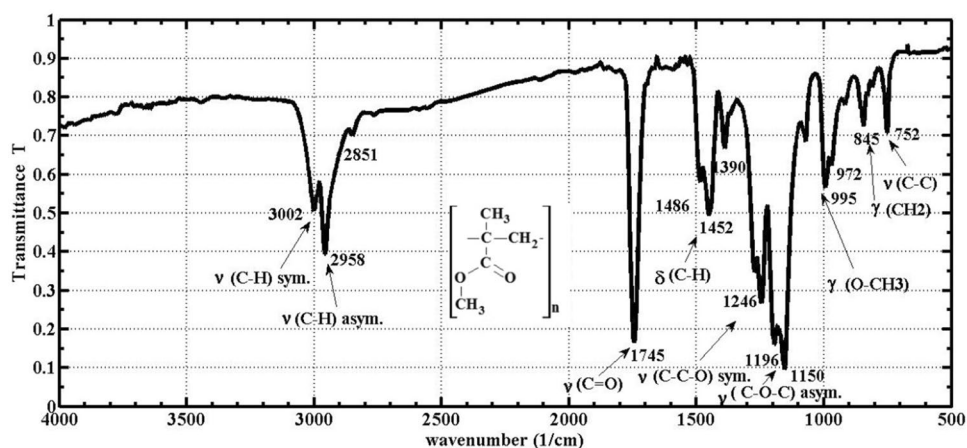
The main absorption bands of the recorded reflection–absorption spectrum, compared with the transmission spectrum of the polymer from the literature are also presented in Table 1 [11, 35, 36].

The reflection–absorption spectra of the superficial PMMA films subjected to different treatments, more or less destructive, are presented comparatively in Fig. 3.

Degradation after heat treatment

The heat treatment of the PMMA film was performed in order to remove the solvent used to prepare the polymer solution to be deposited on the metal substrate. The purpose of heating was not to cause the degradation of the polymer but to remove the remaining solvent [34]. However, slight changes in the appearance of the reflection–absorption spectrum were observed.

Fig. 2 The IRRA spectrum, at 20^0 incidence angle, for a PMMA film, with a thickness of 5.3 μm, deposited on polished steel
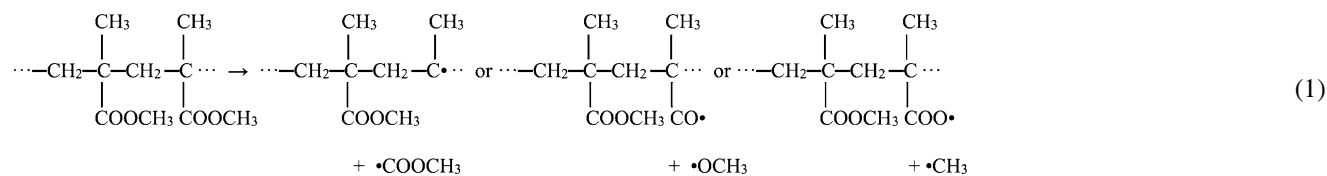
Table 1 The main IR absorption bands of the PMMA

Assignment	Characterization	Transmission spectrum (literature)			Reflection-absorption spectrum
		Ennis and Kaiser [11]	Dybal and Krimm [35]	Schneider et al. [36]	
ν (C–C)	C–C stretch	751	757		752
γ_r (CH2)	CH$_2$ rock	840	843		845
γ_r (O-CH$_3$)	O-CH$_3$ rock		966–989		972
γ_r (O-CH$_3$)	O-CH$_3$ rock				995
ν_a (C–O–C)	C–O–C asym. stretch	1059–1401	1150		1150
ν_s (C–O–C)	C–O–C asym. stretch		1193		1196
ν_s (C–C–O)	C–C–O sym. stretch		1242		1246
ν_s (C–C–O)	C–C–O sym. stretch		1273		1273
τ or ω(CH$_2$)	CH$_2$ wagging or twisting		1367	1370	1369
δ(C-CH$_3$)	C-H deformation		1387	1388	1390
δ(O-CH$_3$)	C-H deformation	1426–1496	1436	1438	
δ(CH$_2$), δ(CH$_3$) and δ (O-CH$_3$)	C-H deformation		1448	1452	1452
δ(C-CH$_3$)	C-H deformation		1485	1483	1486
ν(C=O)	carbonyl stretch	1752	1750		1745
ν(O-CH$_3$)	C-H stretching	2844–3022	2841–3029	2847	2851
ν_a(CH$_2$), ν(C-CH$_3$) and ν(O-CH$_3$)	C-H stretching			2957	2958
ν(C-CH$_3$) and ν(O-CH$_3$)	C-H stretching			2998	3002

The reflection–absorption spectrum of the initial PMMA film with a thickness of 5.3μm, compared to the spectrum of the same film, heat-treated, is shown in Fig. 4.

It was observed that the heat treatment applied does not affect the positions of the absorption bands. The intensity of some absorption bands increases, while others decrease in intensity.
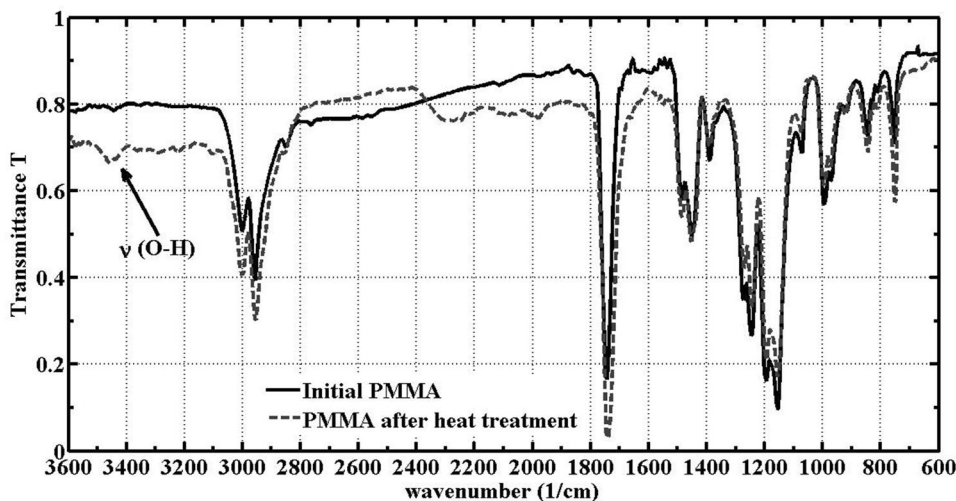
The intensity of the absorption bands corresponding to the links breakage affecting the –CO-OCH$_3$ group decreases. These changes occur due to the cleavage of the ester side groups:

$$
\begin{array}{l}
\cdots\text{CH}_2\text{—C—CH}_2\text{—C}\cdots \rightarrow \cdots\text{CH}_2\text{—C—CH}_2\text{—C}\bullet\cdots \text{ or } \cdots\text{CH}_2\text{—C—CH}_2\text{—C}\cdots \text{ or } \cdots\text{CH}_2\text{—C—CH}_2\text{—C}\cdots
\end{array}
$$

(with CH$_3$ / CH$_3$ substituents and COOCH$_3$ / COOCH$_3$, COOCH$_3$, COOCH$_3$/CO•, COOCH$_3$/COO• groups)

+ •COOCH$_3$ + •OCH$_3$ + •CH$_3$ (1)

Fig. 3 Reflection-absorption spectra of the superficial PMMA films subjected to different treatments

- Initial PMMA
- PMMA after heat treatment
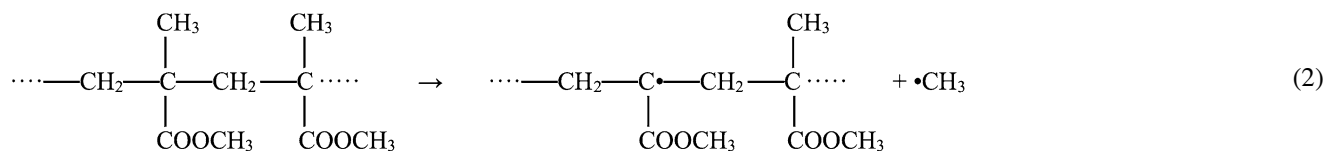- PMMA UV irradiated, 10h
- PMMA gamma irradiated
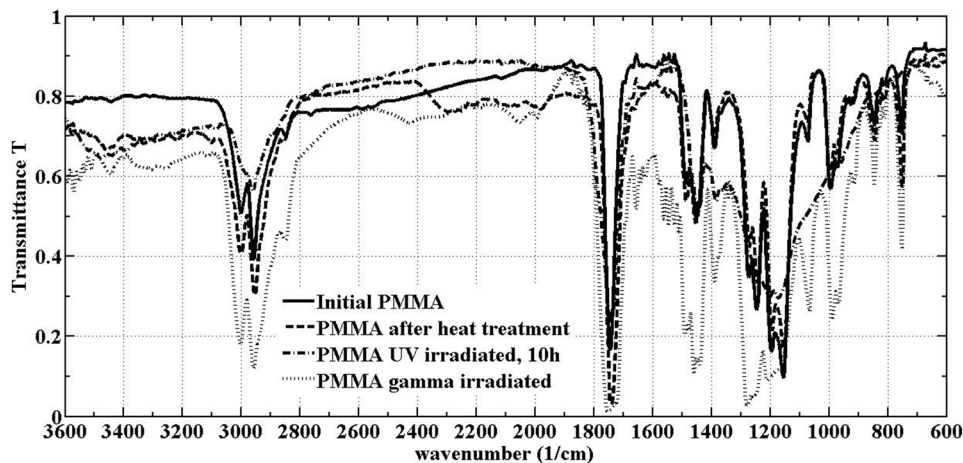
Fig. 4 The reflection–absorption spectrum of the initial PMMA film, compared to the same heat treated film

with the formation of radicals: acetyloxy ($\cdot$COOCH$_3$), methoxyl ($\cdot$OCH$_3$), and methyl ($\cdot$CH$_3$).
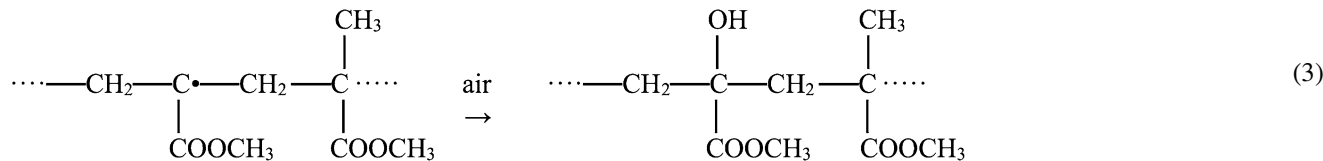
The absorption bands corresponding to γ_r(O-CH$_3$) vibrations from 972 cm^{-1} and 995 cm^{-1} decreases in intensity, also. These changes occur due to the cleavage of the methyl side groups:

$$\cdots\cdots—CH_2—\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}—CH_2—\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\cdots\cdots \quad \rightarrow \quad \cdots\cdots—CH_2—\underset{\underset{COOCH_3}{|}}{\overset{\bullet}{C}}—CH_2—\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\cdots\cdots \quad + \cdot CH_3 \tag{2}$$
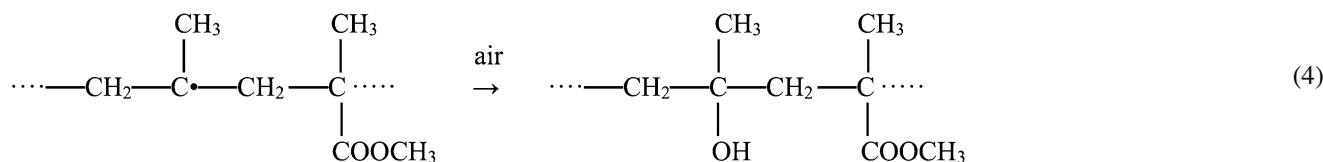
The mechanism for thermal degradation of PMMA has been explained in several papers [1–6].

At the same time, the intensity of the absorption bands corresponding to the asymmetric stretching vibrations C–O–C from 1150 cm^{-1} and 1196 cm^{-1}, respectively to the symmetrical stretching vibrations C–C-O from 1246 cm^{-1} and 1273 cm^{-1}, decreases slightly. The intensity of these bands is affected by the same cleavage of ester side groups.

A slight increase in the intensity of the absorption bands

$$\cdots\cdots—CH_2—\underset{\underset{COOCH_3}{|}}{\overset{\bullet}{C}}—CH_2—\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\cdots\cdots \quad \underset{\rightarrow}{air} \quad \cdots\cdots—CH_2—\underset{\underset{COOCH_3}{|}}{\overset{\overset{OH}{|}}{C}}—CH_2—\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\cdots\cdots \tag{3}$$

corresponding to the C–C or C-H vibrations was observed. Thus, the intensity of the absorption bands corresponding to

vibration from 845 cm^{-1}, the C-H deformation vibrations from 1452 cm^{-1}, and 1486 cm^{-1} and the asymmetric stretching vibrations C-H in the aliphatic group at 2851 cm^{-1} increases slightly.

A slight increase in the intensity of the absorption band at 1745 cm^{-1} corresponding to stretching vibration of C=O also occurs.

The most visible transformations, due to thermal heating in the air, are a slight widening and a significant increase in the intensity of the absorption band at 3443 cm^{-1}, due to the formation of alcoholic polymers containing hydroxyl groups. The tertiary radicals formed after random homolytic scission of main-chain carbon–carbon bonds in the main chain of the polymer can generate polymeric alcohols in the air.

or

$$\cdots\cdots—CH_2—\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}—CH_2—\underset{\underset{}{|}}{\overset{\bullet}{C}}\cdots\cdots \quad \underset{\rightarrow}{air} \quad \cdots\cdots—CH_2—\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}—CH_2—\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\cdots\cdots \tag{4}$$

the C–C stretching vibration from 752 cm^{-1}, the γ_r(CH$_2$) rocking

Fig. 5 The reflection–absorption spectrum of the initial PMMA film, compared to the spectrum of a 1.25 μm thick PMMA film, UV irradiated
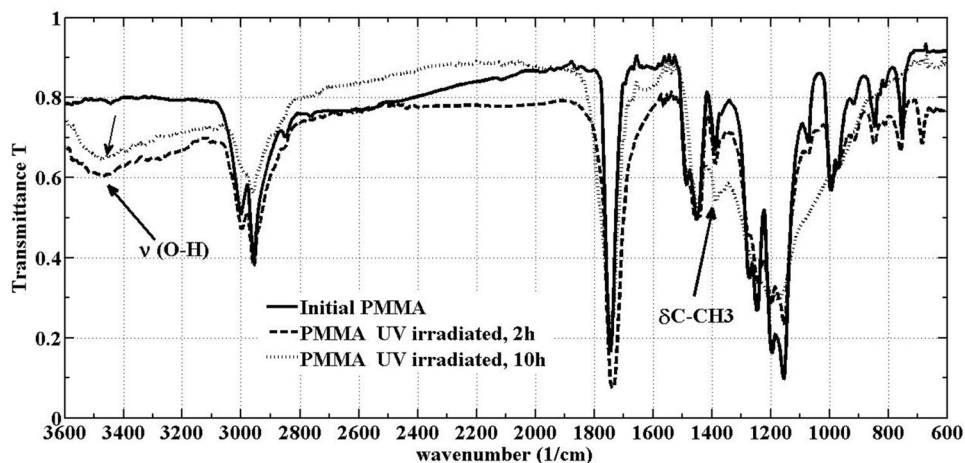
The mechanism of these transformations was explained by Yousif [8].

The heat treatment of the polymer film at higher temperatures or for longer periods of time can severely destroy the structure of the polymer [2, 4, 37, 38]. The PMMA film does not undergo transformations, in the absence of UV radiation, at temperatures below 95^0 C [3].

Thermal stability of PMMA depends on the molecular properties (Mw, Mn, etc.), and on the polymer microstructure (internal defects, type of chain-end groups, etc.). [38].

Degradation with UV radiation

The reflection–absorption spectrum of the initial PMMA film compared to the spectrum of a 1.25 μm thick PMMA film, UV irradiated for 2 and 10 h is shown in Fig. 5.

After a 2 h irradiation, an increase was already observed in the intensity of the absorption band from 3445 cm^{-1} corresponding to the O–H stretching vibration, due to

the formation of alcoholic polymers containing hydroxyl groups, according to the chemical reactions (3) and (4).

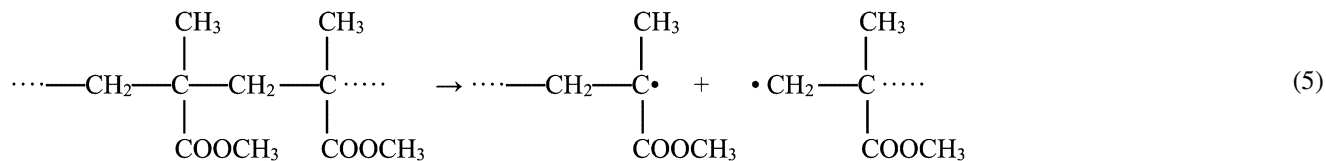At the same time, there is a broadening of this absorption band.

The most visible transformations appear within the spectral region 900–1500 cm^{-1} and are accentuated more and more as the irradiation time increases. These transformations correspond to asymmetric stretching vibrations (C–O–C) within the range 1100–1200 cm^{-1} and symmetrical stretching vibrations (C–C-O) within the range 1200–1300 cm^{-1} [7, 11, 22]. A broadening and an attenuation of the absorption bands were observed. These transformations occur due to the photolysis of the ester side groups and lead to the formation of radicals: $\cdot COOCH_3$, $\cdot OCH_3$, and $\cdot CH_3$, according to the chemical reaction (1).

The absorption band at 752 cm^{-1} corresponding to the skeleton stretching vibrations ν(C–C) moves slightly to higher frequencies and at the same time decreases in intensity as the irradiation time increases. Also, the absorption band from 845 cm^{-1} corresponding to the rocking vibration $\gamma_r CH_2$

Fig. 6 Reflection–absorption spectrum of the initial PMMA film, compared to the γ-irradiated film
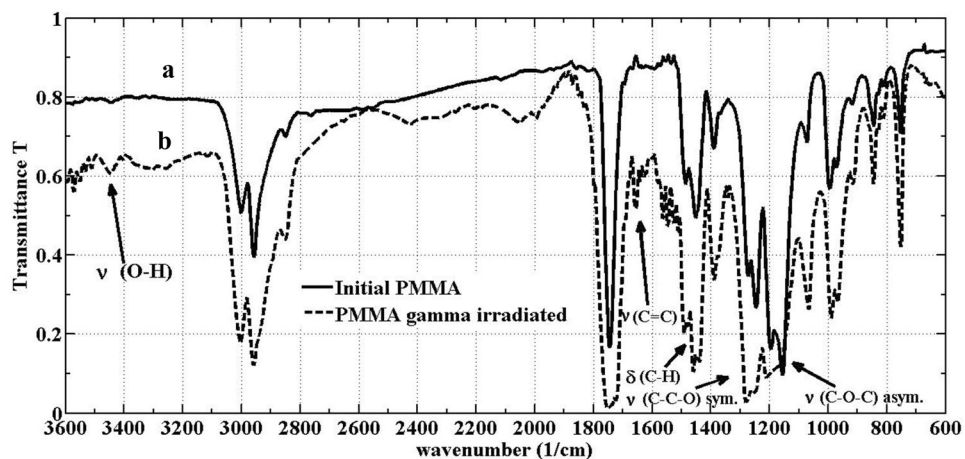
decreases in intensity and disappears during irradiation. The transformations were due to the random homolytic cleavage of main-chain carbon–carbon bonds in the main chain of the polymer:

$$\cdots\!-\!CH_2\!-\!\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\!-\!CH_2\!-\!\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\!\cdots \rightarrow \cdots\!-\!CH_2\!-\!\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\!\bullet \;+\; \bullet CH_2\!-\!\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\!\cdots \qquad (5)$$

and cleavage of the methyl side groups, according to the chemical reaction (2).

A broadening of the absorption band corresponding to the stretching vibration C=O towards lower frequencies occurs when increasing irradiation time with UV radiation. This may be due to aliphatic ketones and aldehydes (which can also be coupled with the double bonds) [8, 39].

Degradation with γ radiation

The reflection–absorption spectrum of the initial PMMA film compared to the spectrum of a γ-irradiated film, with a thickness of 5.53 μm, is shown in Fig. 6. The thickness of the irradiated film was obtained based on interpreting the interference fringes present in the region 2000–3400 cm^{-1} [31].

The irradiation of the PMMA film with radiation γ produces an increase in the intensity of all absorption bands [28].

There is an increase in the intensity of the absorption band from 3443 cm^{-1} corresponding to the O–H stretching vibration due to the formation of alcoholic polymers containing hydroxyl groups, according to the chemical reaction (5).

An increase occurs in the intensity of the absorption bands from 2851 cm^{-1} and 3002 cm^{-1} attributed to the symmetric and asymmetric ν(C-H) stretching vibrations of the methyl carboxyl and methyl chain groups, as well as the main chain of methylene (CH_2) as a result of the photolysis of the methyl side groups and of the ester side groups [28].

The absorption band 1745 cm^{-1} corresponding to the stretching vibration C=O increases in intensity as well.

It was observed that γ radiation significantly affects the absorption bands within the region 700–1700 cm^{-1} [28]. The absorption band at 1656 cm^{-1} attributed to the stretching vibration of the C=C bonds occurs due to the generation of C=C bonds as a result of the cross-linking between the radicals after the initial chain scission or end chain depolymerization (unzipping) [21, 28].
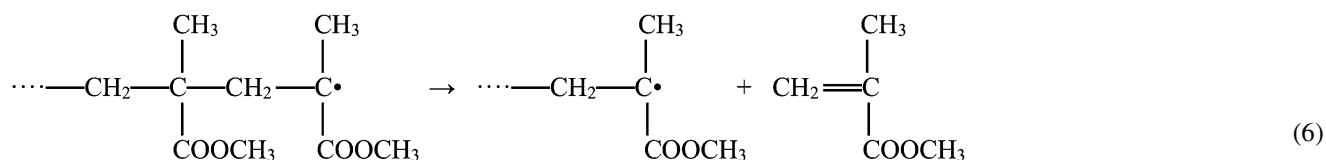
In the spectral region below 1500 cm^{-1} was observed an intensification of all spectral bands associated with different deformation vibrations δ(C-H) of methyl groups, of stretching vibrations ν_a(C–O–C) or ν_s(C–C-O) of methyl carboxyl groups and of skeletal ν(C–C) stretching vibrations. The bands of C-H stretching or deformation vibrations were assigned by Dirlikov et al. to the methylene (CH_2), α-methyl (CH_3) or methyl ester (O-CH_3) groups of the polymer structure [36, 40, 41]. Also increases in intensity and absorption band at 845 cm^{-1} corresponding to rocking vibration γ_r(C–C) [11].

These visible transformations occur due to the photolysis of the methyl side groups and ester side groups and the formation of radicals: acethyloxy (·$COOCH_3$), methoxy (·OCH_3), and methyl (·CH_3), according to the chemical reaction (1).

Conclusion

The PMMA thin films deposited on flat metal mirrors can be investigated with great success by an external reflection spectroscopic technique, called reflection–absorption, in which the recorded quantity is the transmittance. The appearance of the reflection–absorption spectra is very similar qualitatively to the transmission spectrum of the polymer. The visible changes in the appearance of the reflection–absorption spectrum occur during the degradation processes of the PMMA film, as a result of the structural changes of the polymer. The significant changes in the appearance of the spectrum consist of widening the absorption bands, changing their intensity, or shifting the positions of the bands. The cleavage of C-CH_3 bonds and the formation of methyl radicals produce increases in the intensity of the absorption bands corresponding to the stretching or deformation vibration of C-H within the spectral regions 1300–1500 cm^{-1} and 2800–3000 cm^{-1}, respectively. The increase of the band intensity from 1390 cm^{-1} corresponding to the C-H deformation vibrations

$$\cdots\!-\!CH_2\!-\!\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\!-\!CH_2\!-\!\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\!\bullet \rightarrow \cdots\!-\!CH_2\!-\!\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\!\bullet \;+\; CH_2\!=\!\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} \qquad (6)$$

occurs as a result of the formation of $\cdot CH_3$ radicals. The frequencies of the absorption bands from 1452 cm^{-1} and 3002 cm^{-1} will decrease as a result of the weakening of the C-H bonds in the newly formed radicals. The absorption bands within the spectral regions 1300–1500 cm^{-1} and 2800–3000 cm^{-1} respectively, corresponding to the deformation or stretching vibrations C-H from the ester group (O-CH$_3$) were affected as a result of the cleavage of the ester side groups. The breaking of the ester side groups affects the absorption bands corresponding to the symmetrical stretching vibrations (C–C–O) from 1246 cm^{-1} and 1273 cm^{-1}. The absorption bands decrease in intensity and will be shifted to lower frequencies as a result of the weakening of the C-COOCH$_3$ bond. All observations on the reflection–absorption spectra are in agreement with the mechanism of PMMA film degradation, subjected to various types of destructive degradation: thermal heating, UV irradiation or γ irradiation. The degradation of the polymer was all the more accentuated the higher the intensity and duration of the applied treatments. The fact that the same transformations recorded by other techniques of IRRA spectroscopy reported by other authors are observed validates the technique used by us (the IRRA spectrum recorded after a simple reflection).

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