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Polymer 41 (2000) 1981–1988

polymer

# Photooxidation of blends of polystyrene and poly(vinyl methyl ether): FTIR and AFM studies

B. Mailhot*, S. Morlat, J.-L. Gardette

*Laboratoire de Photochimie Moléculaire et Macromoléculaire, UMR CNRS 6505, Ensemble Universitaire des Cézeaux, F-63177 Aubiere Cedex, France*

Received 8 January 1999; received in revised form 5 March 1999; accepted 18 March 1999

## Abstract

The chemical evolution of blends of poly(vinyl methyl ether) and polystyrene in conditions of photooxidation has been studied by infrared spectrometry and the photoproducts formed have been identified. The characterisation of the oxidation kinetics has permitted the detection of interactions between the two polymers. Analysis of the photooxidised samples by AFM has shown that the changes of the surface aspect could be characterised as a function of the irradiation time using several parameters and a tentative correlation between the modifications of the surface and the phase separation with the evolution of the chemical structure is proposed. © 1999 Elsevier Science Ltd. All rights reserved.

*Keywords*: Polystyrene; Poly(vinyl methyl ether); Photooxidation

## 1. Introduction

In conditions of thermal and/or photochemical degradation, polymer blends present different evolutions depending on the miscibility of the components. For example, a study of the thermal degradation of miscible and non-miscible blends of polyester/poly(vinyl chloride) [1] has shown that PVC was stabilised by the presence of polyester in miscible blends. The stabilisation by the polyester component has been explained by a dilution effect: the probability of reaction between the macromolecules that degrade and the species participating in their degradation is reduced. In non-miscible blends, the PVC component degrades independently except at the interface of the two phases.

The material analysed in the present study is a blend of polystyrene (PS) and poly(vinyl methyl ether) (PVME). The two components are miscible in all proportions at ambient temperature. The photooxidation mechanisms of PS [2,3] and PVME [4] have been previously studied in our laboratory. PVME is much more sensitive to oxidation than PS and the rate of photooxidation of PVME is approximately 10 times more than that of PS in our experimental conditions.

The first publications on PS/PVME blends deal with the thermal ageing [5] of the blend. It has been found that the PVME component in the blend appears to age independently of the PS component and is responsible for most the ageing effects measured. However, the PS component would retard the physical ageing processes of PVME in the blend.

Kwei et al. [6,7] have studied the thermooxidation and photooxidation of PS/PVME blends. The authors have measured the oxygen uptake upon irradiation. Thermooxidation and photooxidation processes have a great deal in common: the induction period of the oxidation of PVME is lengthened by the presence of PS, a phase separation occurs and PS, which suffers no decrease in molecular weight itself, experiences chain scissions in the blend.

Since the state of miscibility is a consideration in this study, the phase behaviour of PS/PVME blends will be briefly reviewed. The miscibility of PVME/PS blends have already been extensively studied [8–12]. PS/PVME blends display lower critical solution temperature (LCST) behaviour.

From a thermodynamic point of view, polymers are miscible if they form a single phase [13]. For this to happen, a necessary (though not sufficient) condition is that the free energy of mixing $\Delta G_{\mathrm{mix}}$ be negative. For $\Delta G_{\mathrm{mix}}$ to be negative, a negative heat of mixing is usually required. Strong binary interactions are needed to produce a negative heat of mixing and specific interactions between the two components should be present. (However, if the molecular weights are low, two polymers may be soluble even if they have an endothermic heat of mixing.)

White and Mirau [14] have shown by $^{13}$C NMR that a

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* Corresponding author.

PII: S0032-3861(99)00204-9

specific intermolecular interaction exists between the PS phenyl ring and the PVME methyl group in the solid state that accounts for the blend miscibility.

Moreover, the composition at the surface of PS/PVME films has been shown to be enriched by the PVME component which has the lower surface energy. This was evidenced, among others, by Cowie et al. [15] by ATR FTIR spectroscopy with films of 10 μm of thickness.

On the basis of all these data, the purpose of this study is firstly to compare and complete these results with our photooxidative experiments. Our previous results obtained on the photochemical behaviour of the homopolymers PS and PVME should permit going deeply into the chemical aspects of the degradation in terms of structure of the photoproducts and kinetics of their formation.

In the second part of this paper, we will focus on the analysis of the surface of the samples. Photooxidative ageing induces chemical changes in the blend matrix as well as modifications of the aspect of the materials surface. The surface analysis of the polymer is of great importance during the photoageing for industrial applications. The usual methods used to characterise the evolution of the surface are for example roughness or brightness. The utilisation of AFM technique is presently not developed.

$\gamma$-Irradiated films of polyethylene, polycarbonate [16] and poly(vinyl chloride) [17] were studied by Güven et al. The authors noticed the increase of hill-like structures with irradiation. This increase is shown either as an increase in the size and height of initially existing hills or creation of new craters and hills upon irradiation. The major topological effect of $\gamma$-irradiation is the formation of hills instead of wells. The authors explained this phenomenon by the formation inside the polymers of gaseous products, mainly hydrogen for both PE and PC. The gases force themselves out from the surface causing the formation of irregular protrusions.

No data on the surface analysis of photooxidised PS/PVME blends have been found. However, images of phase separated PS/PVME blends have been published [18–21]. Kajiyama et al. [18,19] observed a phase separation for ultra-thin blends when the thickness of the film was less than twice the radius of gyration of the components. The phase separated PVME/PS 50/50 w/w film showed that circular droplet-like PVME domains of ca. 200 nm diameter and 10–25 nm height were present on the flat PS matrix.

Very recently, Karim et al. [20] observed undulations of the film surface that were apparently caused by variation of the interfacial tension within the plane of the film arising from the phase separation. The elevated regions are behaving like a glassy or very viscous polymer liquid while the flatter and lower regions are less viscous. The authors concluded that the protrusions were made of droplets of dPS-rich phase encapsulated by a thin layer of PVME rich phase (≈5 Å), presumably due to the higher mobility and lower surface energy of the PVME. The degree of connectivity within the plane depends on the stage of phase separation. In the late stages, pinched-off "pancake-shaped" droplets are formed.

So, the second purpose of this article is to try to characterise the surface of the photooxidised films. The modifications of the surface aspect are linked to the chemical evolution of the material in conditions of photoageing. A tentative correlation between the evolution of the roughness measured by AFM with chemical changes occurring in the blends and with the phase separation is presented.

## 2. Experimental section

The PVME (Scientific Polymer Products) was 50% solids in toluene and its approximate molecular weight-average was 95 000 (GPC) ($T_g = -63$°C). The PS ($M_w = 280\ 000$) was obtained from Aldrich ($T_g = 100$°C). Films, of several tens of microns, were obtained by casting from toluene solutions onto KBr plates or onto microscope slides after evaporation of the solvent (for a minimum one week, at ambient temperature). The composition and the thickness of the films and deposits were verified by IR. The thickness was always less than 30 μm.

Irradiations were carried out in a SEPAP 12/24 unit. This apparatus has been designed for the study of the polymer photodegradation in artificial conditions corresponding to a medium acceleration of ageing. It is equipped with four medium pressure mercury lamps. Wavelengths below 300 nm are filtered by a borosilicate envelope. SEPAP 12/24 has been described in several papers (see for example Refs. [22,23]).

The photooxidised samples were submitted to $NH_3$ treatments in order to identify the photoproducts. The films were then exposed to $NH_3$ gas, at room temperature, in a simple flow glass system that could be sealed off to permit the reaction to proceed. Acid groups react with $NH_3$ to give ammonium carboxylates [24]. They are characterised by an infrared absorption band above 1550 $cm^{-1}$. Esters also react with $NH_3$ to produce amide groups. Amide groups present, among others, two characteristic absorption bands around 1670 $cm^{-1}$ (amide I band) and around 1630 $cm^{-1}$ (amide II band).

FTIR spectra were recorded with a Nicolet 760 or a Nicolet 5SX spectrometer, working with Omnic software. Spectra were obtained using 32 scans summations and 2 or 4 $cm^{-1}$ of resolution. All the spectra presented in this paper are non-corrected.

UV–visible spectra were recorded on a Shimadzu UV-2101PC spectrometer equipped with an integrating sphere.

Images acquisition were performed by Atomic Force Microscopy (AFM), in Tapping Mode, on a Nanoscope III of Digital Instruments. The samples were obtained by evaporation of a toluene solution of PVME/PS blend cast on the metallic support adapted for AFM analysis. The

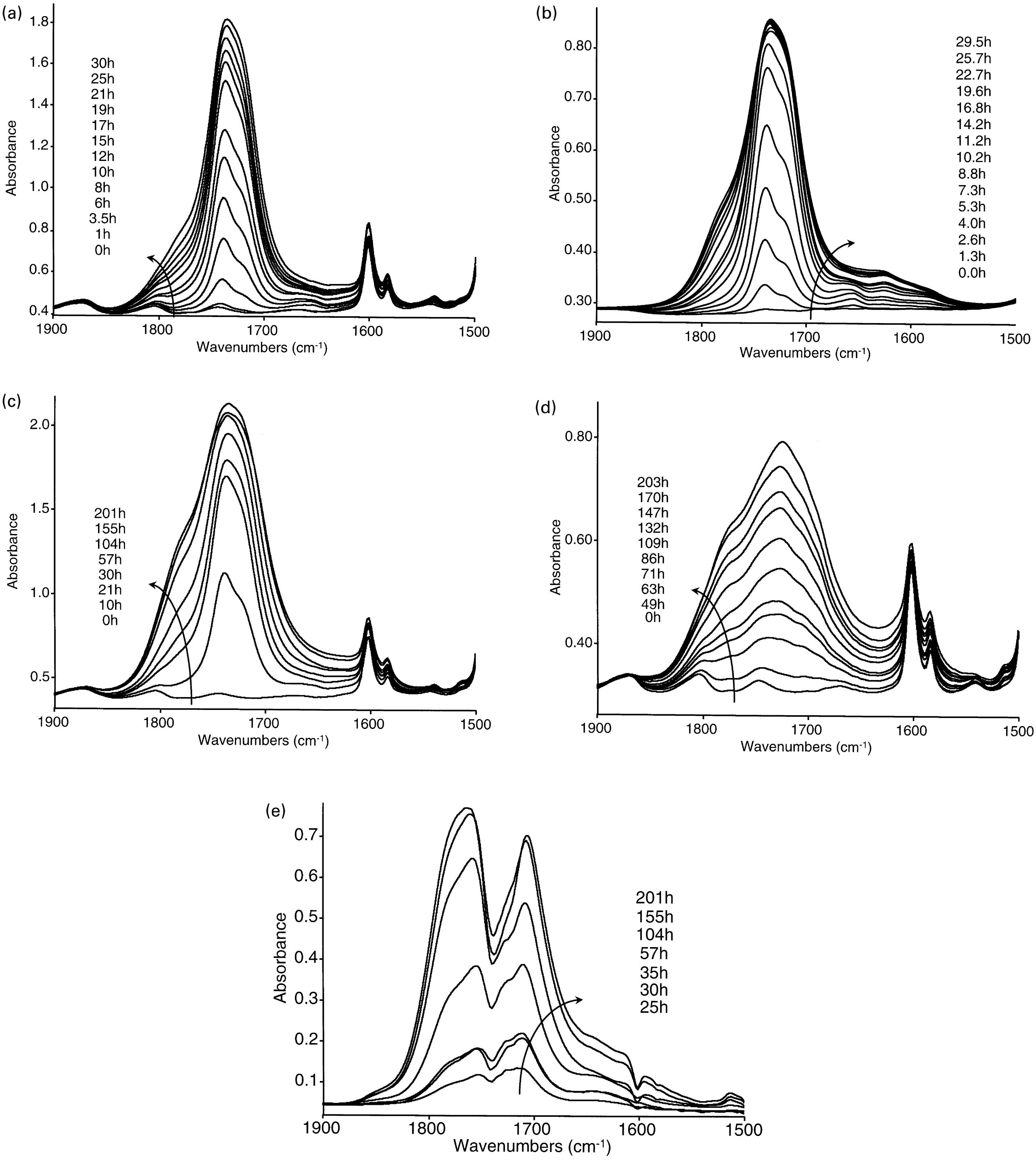


Fig. 1. Evolution of the IR spectra of: (a) PVME/PS 50/50 mol% sample (32 μm) during the photooxidation; (b) PVME sample (9 μm) during the photooxidation; (c) PVME/PS 50/50 mol% sample (32 μm) during the photooxidation; (d) PS sample (13 μm) during the photooxidation; (e) PVME/PS 50/50 mol% sample (32 μm) during the photooxidation (subtraction of spectra between the spectrum of the 21 h irradiated film and the spectra of the film irradiated for a longer duration).

thickness of the deposit has been evaluated to approximately 80 μm. The composition of the PVME/PS blend was 64/36 mol%.

Images of the surface were recorded as a function of irradiation time. For each irradiation time, different regions of the sample were scanned to sustain the reproducibility of the results. Moreover, each image is recorded several times at the same place. Two experiments have been carried out independently and the results obtained in both cases were reproducible.

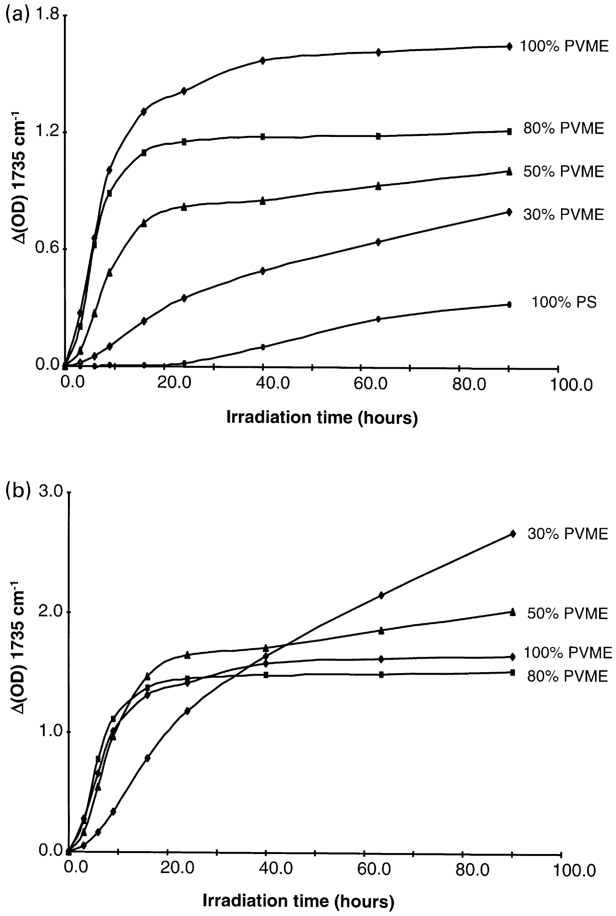


Fig. 2. (a) Variation of absorbance measured at 1735 $cm^{-1}$ in function of irradiation time for deposits of 20 μm thickness for homopolymers PVME and PS and for blends containing 100, 80, 50, 30 and 0 mol% of PVME. (b) Identical to Fig. 2(a) after correction of depth in order to have the same PVME content in each sample.

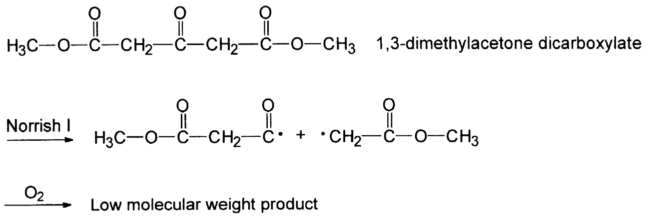
## 3. Results and discussion

### 3.1. Photooxidative behaviour of the blends

#### 3.1.1. Identification of the photoproducts

The behaviour observed by infrared analysis of PVME/PS blends of 50/50 mol% irradiated at $\lambda \geq 300$ nm in the presence of oxygen shows two periods. During the first hours of irradiation, the absorption bands observed are very similar to those observed for pure PVME photooxidised in the same conditions (carbonyl zone presented in Fig. 1(a) and (b). This result indicates that the IR bands observed in the blend reflect mainly the formation of the photoproducts of PVME oxidation. These photoproducts have already been identified [4]. After less than 20 h of irradiation, in similar conditions, the oxidation of PVME homopolymers reaches a limit value and the absorbance corresponding to the oxidation products increases no more. So, after this first period, the modifications of the spectra of the blend (Fig. 1(c)) should reflect the oxidation of pure PS (Fig. 1(d)). In order to verify that the increase of absorbance in this second period could be attributed principally to the formation of photoproducts resulting from the oxidation of PS, a subtraction between the spectrum of the 21 h irradiated film and the spectra of the films irradiated for a longer duration was carried out (Fig. 1(e)).

The shapes of the IR bands are very different from that of the pure PS. The spectra in Fig. 1(e) show that once formed within the first phase, the product at 1733 $cm^{-1}$ progressively disappears in the second phase. This gives a minimum of absorbance in the carbonyl band between 1850 and 1600 $cm^{-1}$. The disappearance of the product at 1733 $cm^{-1}$ increases with the irradiation time, which modifies the shape of the carbonyl band arising from the polystyrene photooxidation. This behaviour is observed in the case of the PVME homopolymer, and after a first phase of oxidation leading to the accumulation of the oxidation products, one can observe a progressive increase of the carbonyl absorbance for longer irradiation times. This reflects the loss of some of the oxidation photoproducts. The band at 1733 $cm^{-1}$ has been attributed to ketonic groups of keto-diesters compounds such as dimethyl malonate or 1,3-dimethylacetone dicarboxylate [4]. These molecular products can migrate out of the polymeric matrix directly or can be photolysed by a Norrish type I reaction of the ketone, which leads to lower molecular weight products that can be lost by migration.



$$H_3C-O-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-O-CH_3 \quad \text{1,3-dimethylacetone dicarboxylate}$$

$$\xrightarrow{\text{Norrish I}} H_3C-O-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}\cdot + \cdot CH_2-\overset{O}{\overset{\|}{C}}-O-CH_3$$

$$\xrightarrow{O_2} \text{Low molecular weight product}$$

The chemical treatment of photooxidised blends by $NH_3$ gas has been carried out in order to verify if the same photoproducts were formed in the blend and in the homopolymers, and eventually to give evidence of the formation of new photoproducts. After reaction with $NH_3$ of a 86 h photooxidised film, an amide band is observed at 1670 $cm^{-1}$ (the maxima formed for the homopolymers PS and PVME were 1669 and 1671 $cm^{-1}$, respectively). The ammonium carboxylate bands were observed approximately at 1590 and 1568 $cm^{-1}$ (large bands). Two maxima were noted in the case of PS at 1585 and 1553 $cm^{-1}$ corresponding, respectively, to aliphatic and aromatic carboxylates. For PVME, the maximum was noted at 1571 $cm^{-1}$. The band at 1568 $cm^{-1}$, resulting from the $NH_3$ treatment of the blend, was progressively shifted to lower wavenumbers when the $NH_3$ treatment was carried out on films of increasing amounts of PS or increasing irradiation time. This band includes the 1553 and 1571 $cm^{-1}$ absorptions.

The $NH_3$ derivatisation reactions of photooxidised films indicate the formation of the same photoproducts as those

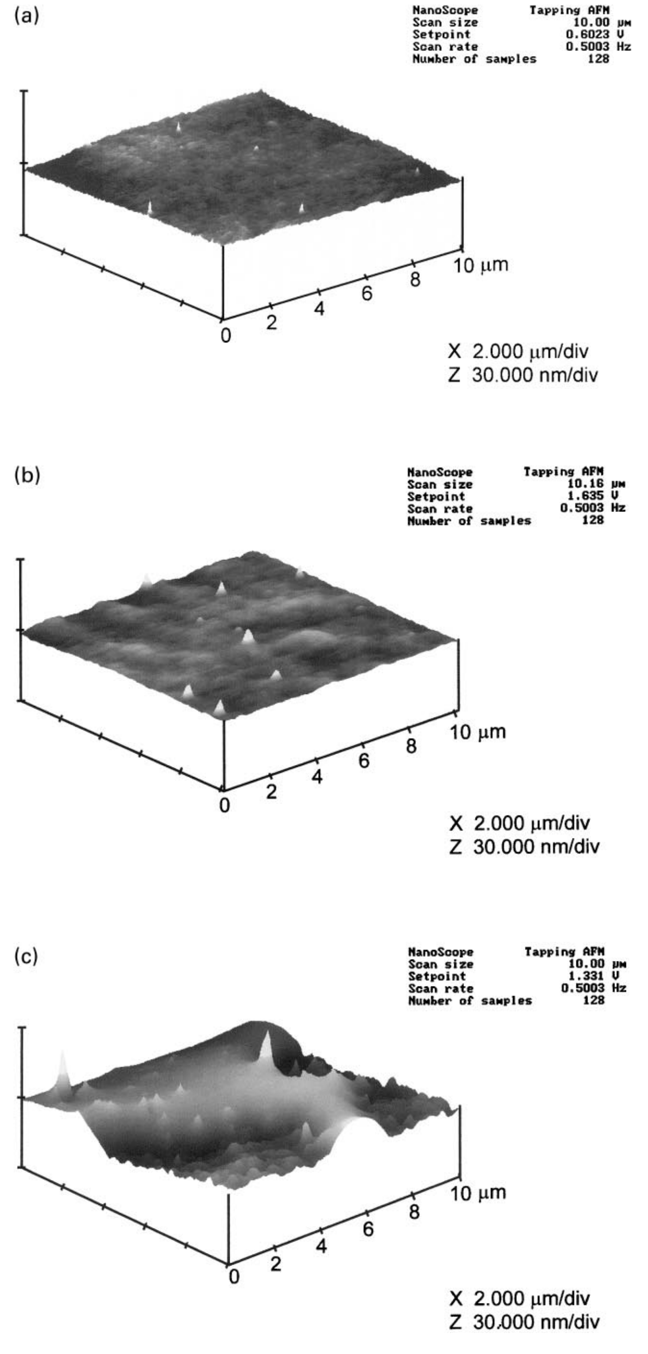


Fig. 3. AFM image of a PVME/PS 64/36 mol% deposit: (a) before irradiation; (b) after 6 h of irradiation; and (c) after 12 h of irradiation.

previously identified in the homopolymers; no new photoproducts could be identified.

For the blends of other compositions, one observed that the photooxidation of PVME rich blends was very close to the photooxidation of pure PVME in terms of structure and relative concentration of the products.

### 3.1.2. Kinetics of formation of the photoproducts

The development of the ester band at 1735 $\mathrm{cm}^{-1}$ was measured as a function of the irradiation time for deposits of 20 µm thickness on KBr plates of homopolymers and blends containing 100, 80, 50, 30 and 0 mol% of PVME (Fig. 2(a)).

The two successive phases of the oxidation described above were observed. During the first 20 h of irradiation, a rapid increase of absorbance was noted in the pure PVME and in the PVME rich blends. This trend can be correlated with the formation of the oxidation photoproducts of the PVME macromolecules. After this period, the absorbance became nearly constant.

For pure PS, the absorbance increases slowly and reaches a lower value similar to that measured for PVME, even for long irradiation times. Conversely to Kwei et al. [6,7], no induction period was detected.

The absorbance measured at 1735 $\mathrm{cm}^{-1}$ has been corrected by a multiplication factor in order to compare the same quantity of PVME in the blends. For example, the absorbance of the 50/50 mol% PVME blends has been multiplied by a factor 2 to have the same quantity of PVME as in the 100% PVME blend (Fig. 2(b)). Then, one can note that for blends of 80 and 50 mol% of PVME, the extent of oxidation is proportional to the PVME content. For the 30 mol% PVME content, the rate of oxidation is reduced in comparison to pure PVME during the first 30 h of irradiation. After this period, the increase of absorbance is attributable to the oxidation of PS. Therefore, the PS macromolecules are suspected of playing a role in the photooxidation of the PVME macromolecules in PS rich blends.

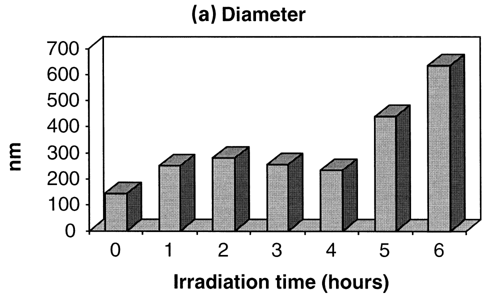
Parallel photooxidation experiments were carried out on deposits of blends of the same composition. The kinetics of oxidation was proportional to the thickness and the reproducibility was of approximately 80%.

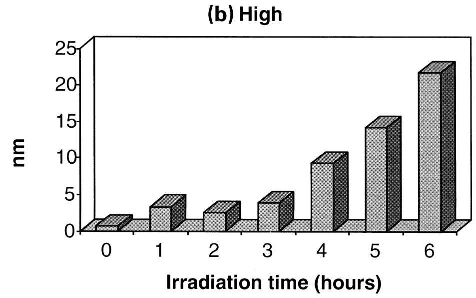
Moreover, it has been noted that the photooxidation of the PS macromolecules starts earlier in the blends than in the pure PS. This result was deduced from the behaviour of the band at 1515 $\mathrm{cm}^{-1}$, characteristic of a PS photoproduct [2]. The higher the percentage of PVME, the earlier the band at 1515 $\mathrm{cm}^{-1}$ develops. These results indicate that the photooxidation of the PS macromolecules should be accelerated by the presence of PVME.

## 3.2. Surface analysis

Irradiation usually leads to noticeable changes of the surface aspect of the polymers. In order to characterise the development of the surface, images of the surface were recorded in function of irradiation time with an atomic force microscope.

Fig. 3(a) represents the surface of the sample before irradiation. This surface is flat and some hill-like structures are observable. The number of hills observed per $\mu\mathrm{m}^2$ depends on the preparation of the sample. On average, the samples analysed contained approximately six peaks per 10 $\mu\mathrm{m}^2$. These structures may not be assumed as impurities since their number and their height increase upon irradiation





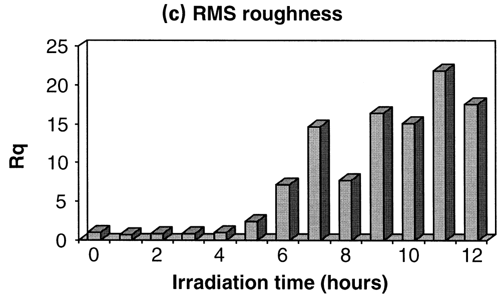


Fig. 4. Variation of the diameter and the high average of the hill-like structures (a) and the RMS roughness parameter (b) in function of irradiation time for a PVME/PS blend of 64/36 mol%.

(Fig. 3(b)). As the irradiation time increases, the images recorded in the different regions of the sample are less and less reproducible. In addition to the growth of hills, the whole surface becomes irregular (see for example Fig. 3(c)).

The diameter and the high average of the hill-like structures has been reported as a function of irradiation time (Fig. 4(a)). The average has been calculated with the measurement of minimum 30 hills, belonging to images recorded in different regions of the sample. Diameter and height increase gradually upon irradiation.

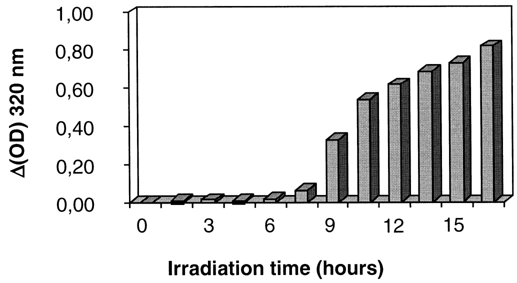


Fig. 5. Evolution of absorbance measured at 320 nm in function of irradiation time for a film of 39 μm thickness for a PVME/PS blend containing 64 mol% of PVME.

A similar explanation to that given by Güven et al. [16] may be envisaged for the photooxidation of the PVME/PS blends since many gaseous products are formed upon irradiation [3,4].

However, the dimensions of the hill-like structures have been evaluated at 150–600 nm diameter and 3–20 nm of height. So, the hill-like structures whose formation has been highlighted by the choice of the *z*-axis scale, look in reality more like circular droplets. The diameter of these droplets is of the same size order as the droplets observed for phase separated blends [18].

As a consequence, the presence of some droplets on the surface of the PVME/PS blends may be also envisaged. These droplets are dispersed at the surface of the homogeneous phase of the blend. Before irradiation, the number of droplets is very small (ca. six per 10 $\mu m^2$) [18] compared to a phase separated sample (more than 300 droplets per 10 $\mu m^2$). The height of the droplets observed before and during photooxidation is less than the height measured by Kajiyama et al. [18]. However the stage of phase separation may be different and the authors had made the measurements on very thin films (25 nm thick). The samples described in this paper have a thickness around 80 μm.

According to Kajiyama et al., the droplets may comprise PVME macromolecules. More recently, Karim et al. [20] have confirmed the presence of droplets in phase separated samples, but they assigned them to a PS rich phase encapsulated in a PVME rich phase.

After 6 h of irradiation, the number of droplets is too high and their sizes are too different to evaluate average diameter and height. For that reason, we used the roughness parameters to characterise the surface. The root mean square (RMS or $R_q$) roughness is the standard deviation of the $Z$ values within the given area and is calculated by the software as

$$\mathrm{RMS} = R_q = \sqrt{\frac{\sum (Z_i - Z_{ave})^2}{N}},$$

where $Z_{ave}$ is the average of the $Z$ values within the given area, $Z_i$ the current $Z$ value and $N$ the number of points within the given area.

The RMS values have been determined in function of irradiation time (Fig. 4(b)). Significant changes of the roughness were observed after 5–6 h of irradiation. After 12 h of irradiation, the roughness of the sample was too well developed and images of 10 $\mu m^2$ were no longer representative of the sample.

### 3.3. Phase separation

The increase of the size of the droplets upon irradiation suggests that photooxidation progressively induces a phase separation by enrichment of the droplets constituted by PVME [18,19] or by a PVME/PS blend rich in PS [20].

The phase separation is usually characterised by the measurement of the cloud point that corresponds to the appearance of turbidity in the film [25]. The measurement of the percentage of transmission (or absorbance) by UV–visible spectroscopy may also reflect the turbidity of the film. On the spectra of PVME/PS blends, no maxima or shoulders are observed but a general increase of absorbance above 250 nm is noted. The changes of the optical density measured at 320 nm as a function of irradiation time are represented in Fig. 5. An increase of absorbance is noted after 6 h of irradiation. The visual observation of the turbidity of the film also permits locating the cloud point at approximately 6 h of irradiation.

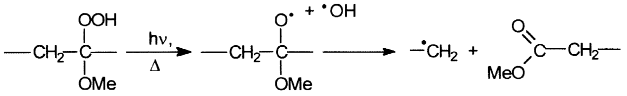
## 4. Discussion

The analysis of the nature of the photoproducts formed upon irradiation in the blends has shown that these products are similar to those identified in the homopolymers. No evidence of the presence of photoproducts formed specifically in the blends was obtained. However, the two components PVME and PS interact and the measurement of the kinetics of oxidation gives evidence that the PVME macromolecules are more stable in the PS rich blends and conversely, oxidation of PS macromolecules is enhanced in PVME rich blends.

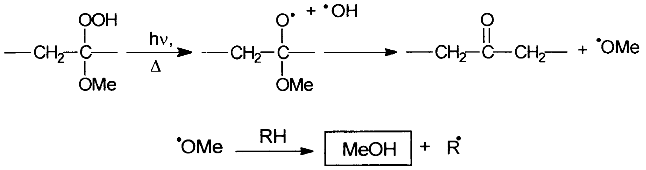
Similar results were obtained by Kwei et al. [6,7]. They observed that, during photooxidation, the steady-state rate of oxidation was proportional to the PVME content for the 70% PVME blend, but for the 50 and 30% blends, the oxidation was several fold smaller than the value expected from the PVME content. The authors suggested that the lower segment mobility in the PS rich blend might be responsible for the slower rate of propagation reaction and phase separation. The authors have also envisaged a reaction occurring between PVME radicals and PS, most likely through the abstraction of the tertiary hydrogen atom of PS. The resulting PS radical, being less reactive in propagation, retards oxidation. Unfortunately, there is no experimental evidence to confirm this proposal and further experiments should be carried out to get more information on the interactions between the two components.

Our experimental results show that, in the first 20 h of irradiation, the photochemical behaviour of the blend could be related to that of PVME. To get a better comprehension of the results of the surface analysis and to try to explain the phase separation phenomenon, a correlation should be done with the formation of PVME photoproducts in the blend. A comparison should be effectuated with the IR results obtained for the PVME homopolymer [4].

In the first 5–6 h of irradiation, the small droplets initially observed at the surface of the blend are growing upon photooxidation. These droplets may indicate the early beginnings of the phase separation. The IR analysis of the photooxidation of PVME homopolymer has shown that during the first 6 h of irradiation an important increase of a band at 3290 $cm^{-1}$ was observed. This band has been attributed to tertiary hydroperoxides. For prolonged irradiations, the hydroperoxides absorption band decreases. The decomposition of hydroperoxides leads to the formation of acetates:



The decomposition of hydroperoxides also produces chain ketone and methanol:



Since phase separation is not initiated by a chain scission which favours solubility, the second way of decomposition of hydroperoxides may be suspected. As recalled, it has been shown that specific intermolecular interactions between the PS phenyl ring and the PVME methyl group in the solid state could account for the blend miscibility. Since the decomposition of hydroperoxides is leading to the loss of the methoxy groups, the oxidised PVME macromolecules could be less miscible in the PS macromolecules.

Since the PVME macromolecules are degraded during the early stages of photooxidation, the formation of the droplets could result from an enrichment by the PS macromolecules, even if their mobility is reduced compared to the mobility of PVME.

After 5–6 h of irradiation, a maximal concentration of hydroperoxides is reached and the phase separation occurs. The size of the droplets probably reaches a limit and then, the roughness increases significantly. The irregularity of the surface may be explained by the formation of oxidation photoproducts on the backbone of the macromolecules and by the formation of gaseous photoproducts that migrate from the sample.

The AFM experiments were done with a 64/36 mol% blend. Some more AFM experiments should be done with different blend compositions, particularly for rich PVME and rich PS contents. Since the kinetics of oxidation are influenced by the composition, the aspect of the surface should also be analysed in function of the composition of the blend.

## 5. Conclusion

The FTIR analysis has permitted the identification of the oxidation products formed upon irradiation and has confirmed that PVME photooxidation is the main cause of the degradation of the blends. Moreover, PVME influences the photooxidation of PS and vice versa.

By AFM analysis, we have shown that the modifications of the surface aspect can be characterised as a function of the irradiation time using different parameters. This method is well equipped to detect the changes that occur during the early stages of the oxidation and may have a lot of applications for other polymers.

Moreover, a good knowledge of the photochemical evolution of the blend has permitted establishing a correlation between the modifications of the surface and the modifications of the chemical structure of the macromolecules resulting from irradiation. Even if some questions are not totally resolved, this preliminary work opens new ways for the study of polymer photodegradation.

## References

[1] Goulet L, Prud’homme RE. Eur Polym J 1986;22:529.
[2] Mailhot B, Gardette JL. Macromolecules 1992;25:4119.
[3] Mailhot B, Gardette JL. Macromolecules 1992;25:4127.
[4] Mailhot B, Morel S, Gardette JL. Polym Degrad Stab 1998;62:117.
[5] Cowie JMG, Ferguson R. Macromolecules 1989;22:2307.
[6] Park H, Pearce EM, Kwei TK. Macromolecules 1990;23:434.
[7] Chien YY, Pearce EM, Kwei TK. J Polym Sci, Part A: Polym Chem 1991;29:849.
[8] Nishi T, Wang TT, Kwei TK. Macromolecules 1998;21:3296.
[9] Ubrich JM, Larbi FBL, Halary JL, Lonnerie L, Bauer BJ, Han CC. Macromolecules 1986;19:810.
[10] Lee HK, Kang CK, Zin WC. Polymer 1997;38(7):1595.
[11] Rice DM, Karasz FE. Polymer 1993;34(1):214.
[12] Abtal E, Prud’homme RE. Polymer 1993;34(22):4661.
[13] Turi EA. Thermal characterization of polymeric materials, vol 1: thermal properties. 2. New York: Academic Press, 1997.
[14] White JL, Mirau P. Macromolecules 1993;26:3049.
[15] Cowie JMG, Devlin BG, McEwen IJ. Polymer 1993;34(3):501.
[16] Güven O, AlaÇakir A, Tan E. Radiat Phys Chem 1997;50(2):165.
[17] Tan E, AlaÇakir A, Uzun C, Güven O. Radiat Phys Chem 1995; 46(4–6):897.
[18] Tanaka K, Yoon JS, Takahara A, Kajiyama T. Macromolecules 1995;28:934.
[19] Kajiyama T, Ohki I, Tanaka K, Ge SR. Proc Japan Acad Ser. B 1995;71:75.
[20] Karim A, Slawecki TM, Kumar SK, Douglas JF, Satija SK, Han CC, Russell TP, Liu Y, Overney R, Sokolov J, Rafailovich MH. Macromolecules 1998;31:857.
[21] Katzen D, Reich S. Europhys Lett 1993;21(1):55.
[22] Lemaire J, Arnaud R, Gardette JL. Rev Gen Caoutch Plast 1981;87:613.
[23] Ly T, Sallet D, Lemaire J. Macromolecules 1981;15:1437.
[24] March J. Advanced organic chemistry. Tokyo: McGraw-Hill-Kogakusha, 1977.
[25] McHerron DC, Wilkes GL. Polymer 1993;34(19):3976.