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Photo-DSC I: A new tool to study the semi-crystalline polymer accelerated photo-ageing

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Abstract

Photo-DSC was used, to study, in situ, the photo-ageing of polycyclo-octene which is a semi-crystalline elastomer. The 'crystallizability', which is the ability of the polymer to crystallize, was tightly dependent on the exposure time and was used to follow the photo-ageing.

The irradiation system of photo-DSC was also compared with a usual accelerating device and no difference was detected in the chemical alteration of the polymeric matrix. Meanwhile, with photo-DSC, the photo-ageing was accelerated compared to a usual accelerating device. By using photo-DSC, atmosphere, exposure time, light intensity and ageing temperature were accurately controlled.

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Keywords: Photo-DSC; Photo-ageing; Cross linking

1. Introduction

Photo-oxidation is the most common cause of polymer degradation in outdoor conditions. Light-polymer interactions lead to drastic changes in the physical and chemical properties of the material. Many studies have been devoted to the comprehension [1,2] and the prediction of complex phenomena occurring upon the photo-ageing of the polymer.

Since the evolution of natural ageing requires a very long time, some accelerated photo-oxidation devices were proposed. SEPAP [3], SunTest [4], Xenotest [5] and WeatherOmeter [6] are the most commonly used. These apparatus aimed:

(i) to create known, representative and well defined experimental conditions of the ageing, notably in terms of irradiation temperature, nature of atmosphere, moisture, etc.
(ii) to accelerate the ageing by increasing light intensity, temperature or both of them.

The common characteristic of these devices is that the irradiation stage is disconnected from the ageing assessment. Usually, the sample is irradiated, removed from the exposure device and analyzed by none destructive methods such as IR spectroscopy. In this work, we propose to combine the exposure and the analysis of the polymer sample in situ inside the DSC furnace.

This technique, photo-DSC, is largely used to follow photo-polymerization and photo-cross linking of photosensitive materials [7–12]. The exothermicity of these reactions allows their study by DSC measurements. In the case of photo-ageing, the light beam will provoke the photo-degradation of the polymeric material while the DSC will be used to measure the thermal consequences.

Semi-crystalline polymers exhibit an ordered part surrounded by an amorphous matrix. Multiple chain-scissions and cross-linking phenomena occur as consequences of the polymer photo-ageing. The mobility of the macromolecular chains is very sensitive to these morphological alterations: The chain-scissions increase the degree

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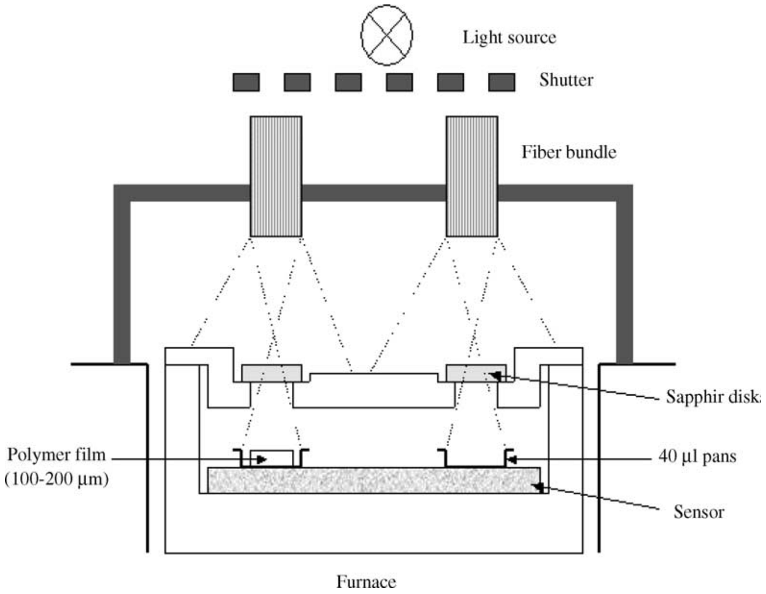

Fig. 1. Photo-DSC system.

of freedom, whereas the cross linking reduces the ability of moving. When a semi-crystalline polymer is cooled from a melted state, its ability to crystallize depends on the macromolecular chain mobility. In a previous paper [13], we showed that the 'crystallizability', which is the ability of the polymer to crystallize, decreased drastically when the material was chemically cross linked. Both heat and temperature of crystallization fell when the curing time of the polymer/dicumyl peroxide mixture increased. The DSC furnace was also used to carry out, at the same time, the curing of the polymer and the measurement of the crystallizability. In this work, an identical approach will be applied to polycyclo-octene, a semi-crystalline polymer: After each light exposure time, the sample is melted and cooled in order to record its crystallization exotherm. Moreover, in this first paper, we mainly intend to define the operational conditions in terms of light intensity, temperature, atmosphere and time exposure in order to use the photo-DSC combination as a tool to study the accelerated photo-ageing.

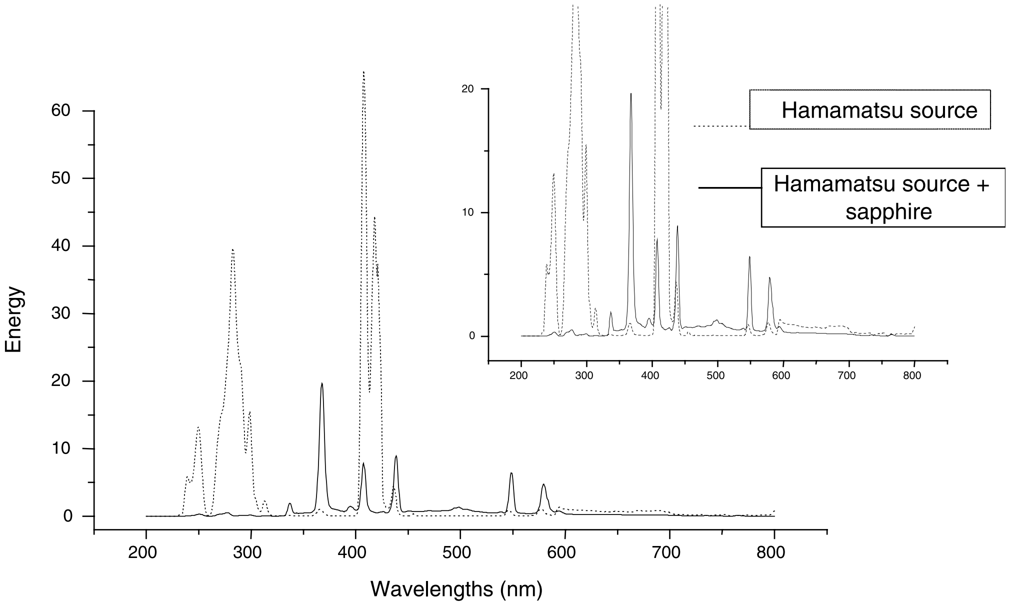

Fig. 2. Hamamatsu source spectra: Before (···) and after filtration through the sapphire disks (—). After filtration, the source supplies radiation of wavelengths longer than 300 nm representative of outdoor ageing.

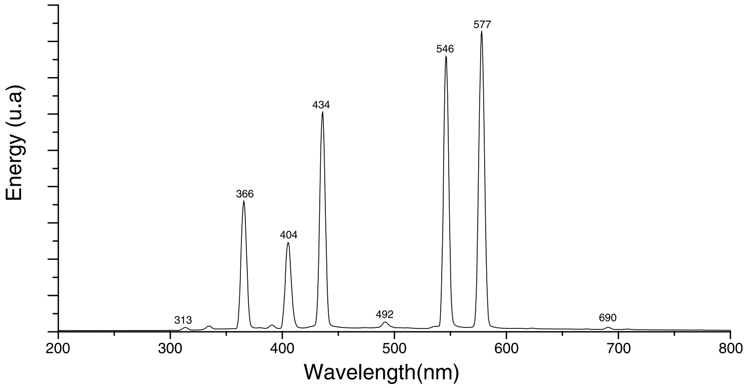

Fig. 3. Emission spectrum of the filtered ‘medium pressure’ Hg source equipping the accelerating photo-oxidation SEPAP device.

2. Experimental part

2.1. Materials

Polycyclo-octene (–[CH_2–CH_2–CH_2–CH_2=CH_2–CH_2–CH_2–CH_2–]$_n$), also named Vestanemer, was supplied by Hüls Company. It was purified twice by two successive re-precipitations into methanol from a chloroform solution in order to remove the traces of process stabilizers. From NMR analysis the microstructure was 21 and 79% of *cis* and *trans* stereoisomers, respectively. By SEC determination, its molecular weight was 42,100 and 118,100 g/mol as M_n and M_w, respectively (2.8 as polydispersity index). DSC measurement shows that it is a semi-crystalline elastomer (30%) with −61 °C as glass transition temperature (T_g), 60 °C as melting temperature (T_m) and a crystallization temperature (T_c) around 30 °C. A film of 100–200 μm in thickness was prepared by using a heating laboratory press. The pressure was 19 Mpa and temperature 145 °C for 1 min. The absence of thermal oxidation was checked by IR spectroscopy and also by solubility test. No carbonyl or hydroxyl signals were detected and the elastomer film was still completely soluble in chloroform. Nitrogen and oxygen gases were of ‘ultra pure’ quality. The compressed air was cleaned and dried before used as experimental atmosphere inside the DSC furnace.

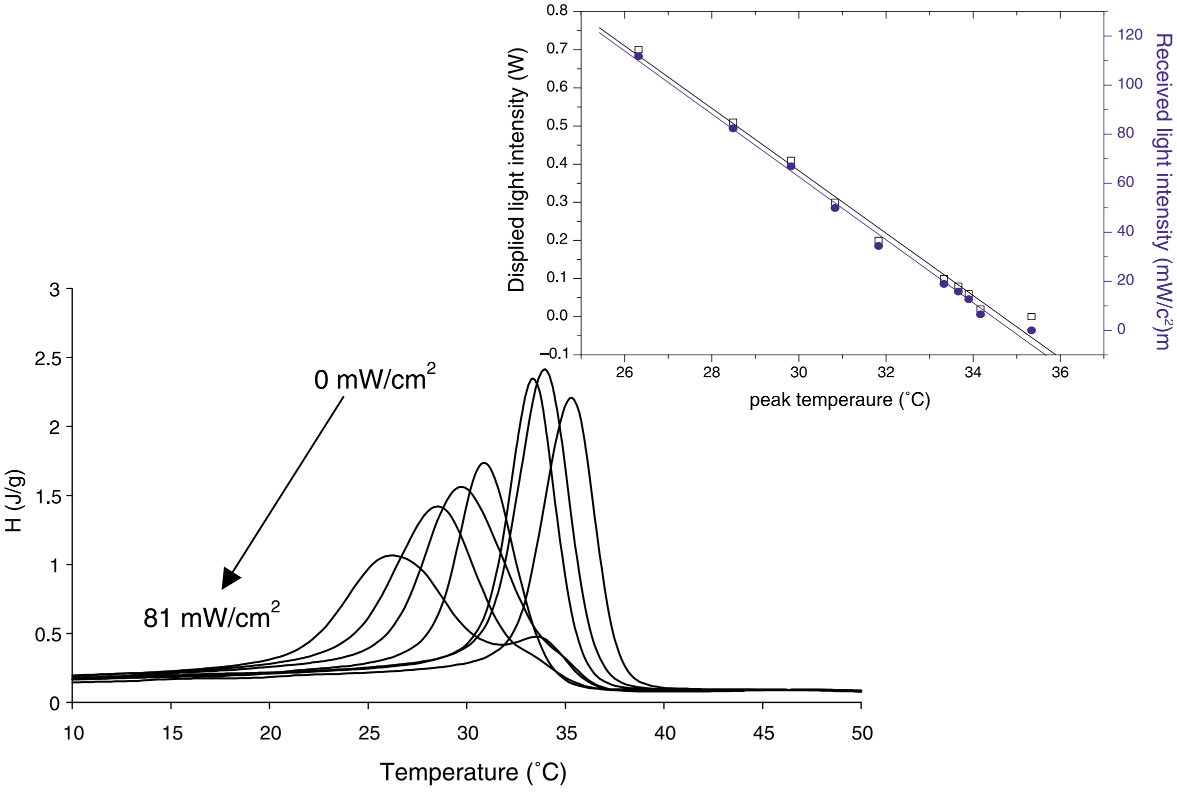

Fig. 4. Exotherms of anisothermal crystallization (10 °C/min) of Vestanamer film irradiated at 60 °C at various light intensity (0–81 mW/cm^2). The exposure time was 10 min for each irradiation. The work atmosphere was air.

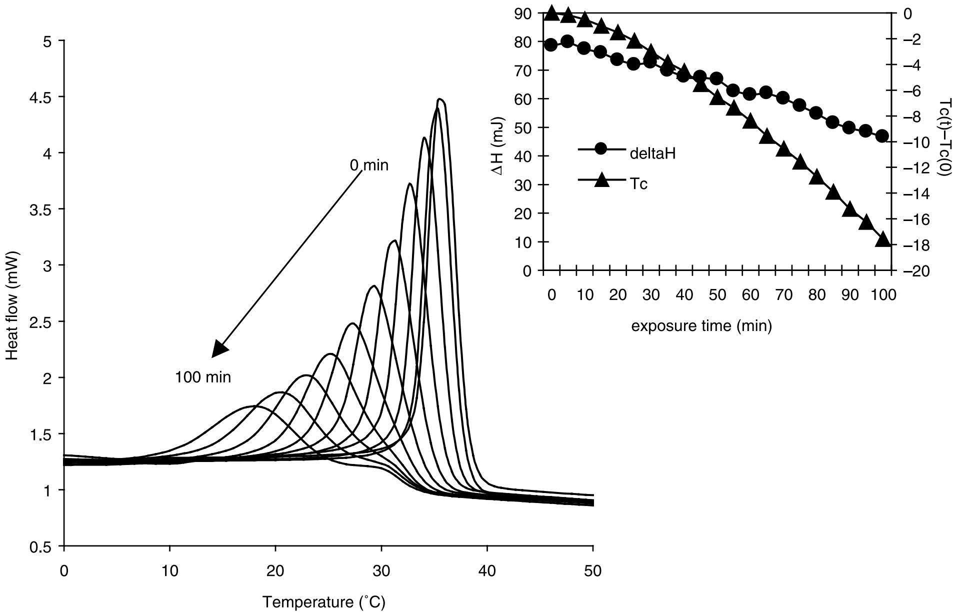

Fig. 5. Anisothermal crystallization (10 °C/min) of Vestanemer irradiated at 6.5 mW/cm^2, 35 °C and under air atmosphere. Exposure times range from 0 to 100 min. In the insert, temperature (T_c) and heat (ΔH) of crystallization versus exposure time are plotted.

2.2. Photo-DSC system

A Mettler Toledo DSC822^e apparatus, equipped with an Intracooler and a liquid nitrogen cooling set, was used. It allows working between 500 and −150 °C with a scanning temperature rate from 0.1 °C/h to 50 °C/min. Indium (156.61 °C), zinc (419.58 °C) and heptane (−90.61 °C) were used to calibrate this apparatus. A Hamamatsu light generator equipped with a 'Lightningcure LC6' source (Xe/Hg, 'medium pressure') was affixed to the DSC device as represented on Fig. 1. The light generator is servo-controlled by the DSC software (STARe) which permits a choice of both the light intensity from 0 to 324 mW/cm^2 and the duration of the irradiation. Two identical fiber bundles supply the irradiation light both to sample and reference DSC pans. The source, filtered by the sapphire disks, delivers radiations of wavelengths longer than 300 nm, representative of outdoor ageing (Fig. 2).

2.3. SEPAP device

The set up, already described elsewhere, was based on a 'medium pressure' mercury source filtered by borosilicate envelope (Mazda type MA 400) supplying radiation of wavelengths longer than 300 nm. Fig. 3 gives the emission spectrum of this source. A laboratory version of SEPAP-ATLAS® was used in this work. The source was located along the focal axis of a cylinder with an elliptic base. At the other focal axis, the samples were fixed on a rotating carousel. The temperature was regulated at 35 °C. Films were removed and analyzed after various exposure times.

A Nexus IR spectrophotometer, supplied by Thermo-Optec was used to carry out the IR analysis of the photo-irradiated samples.

3. Results

3.1. Crystallinity changes

Vestenamer sample of 150 μm thick (2 or 4 mg) is set in a DSC pan and undergoes the following procedure: 2 min at 60 °C without irradiation to make sure that the polymer is completely melted, 10 min of exposure at 60 °C with a light intensity ranging from 0 to 81 mW/cm^2.

After this exposure time, the sample is cooled down to 10 °C with a rate of 10 °C/min in order to record its crystallization signal. Fig. 4 shows that crystallization thermograms undergo drastic change when the light intensity increases. Both temperature and heat of crystallization decrease when the light intensity increases. In this figure, the displayed values (left scale, in W) and the intensity received by the sample (right scale, in mW/cm^2) are also plotted against the crystallization peak temperature. A linear correlation is obtained.

In Fig. 5, the crystallinity changes are represented as a function of exposure times at given light intensity (6.5 mW/cm^2). After 2 min in darkness, a polymer film sample, maintained at 35 °C, was irradiated for 5 min and then heated to 60 °C to be melted and finally cooled down to 0 °C to record its crystallization exotherm. The same sample underwent the same procedure several times. Consequently, the exposure times increased by increments of 5–100 min.

As shown in the insert, the crystallization heat (ΔH) and temperature (T_c) continuously decrease with irradiation

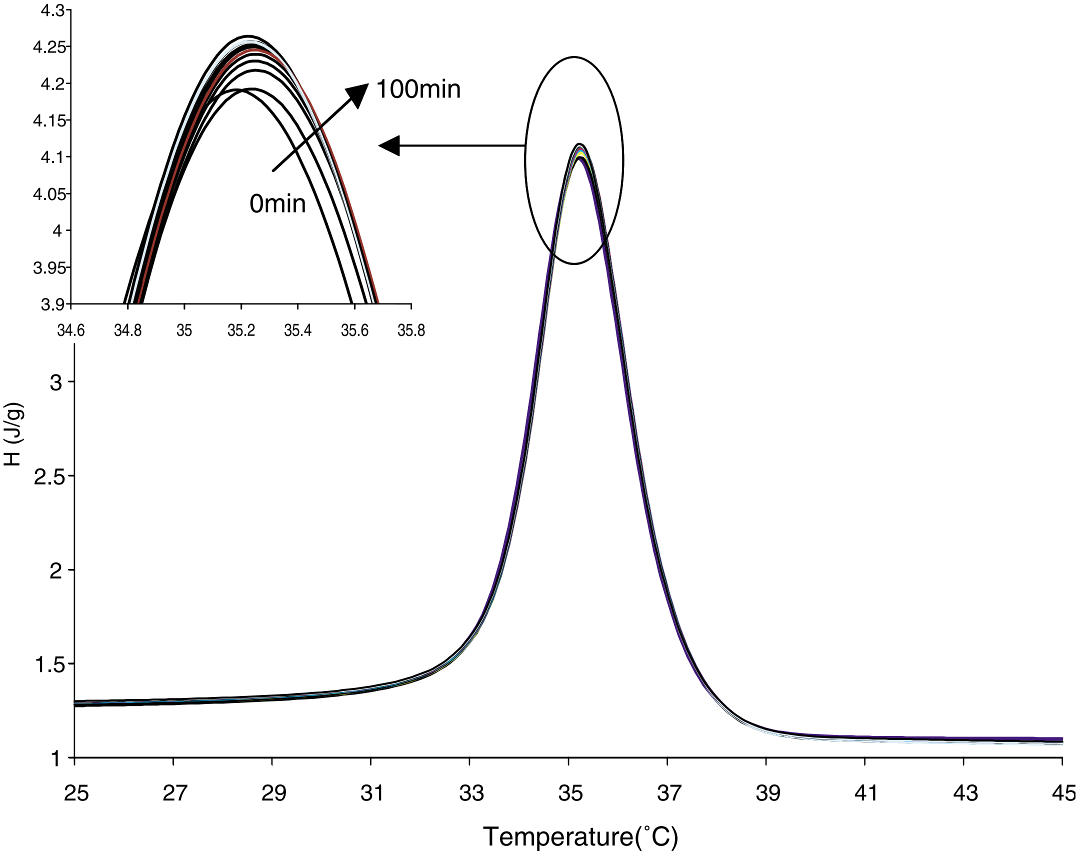

Fig. 6. Anisothermal crystallization (10 °C/min, air) of Vestanemer maintained at 60 °C without irradiation. Exposure times range between 0 and 100 min.

times. The rate of this reduction increases with the exposure temperature as it was verified at 60 °C (results not exhibited here).

At 60 °C, Vestanemer is melted and, under the oxidizing atmosphere, thermal oxidation may occur. Fig. 6 shows the crystallization exotherms, recorded according to the same previous experimental procedure but without light exposure. As it can be noted, no significant changes are noticed. So, thermal oxidation seems to be negligible at 60 °C and all the crystallinity changes are attributed to photo-ageing phenomena.

3.2. Role of the atmosphere composition

The composition of the atmosphere surrounding the polymeric sample can be controlled. Fig. 7 shows the changes in the crystallization temperature ($T_c(t) - T_c$) as

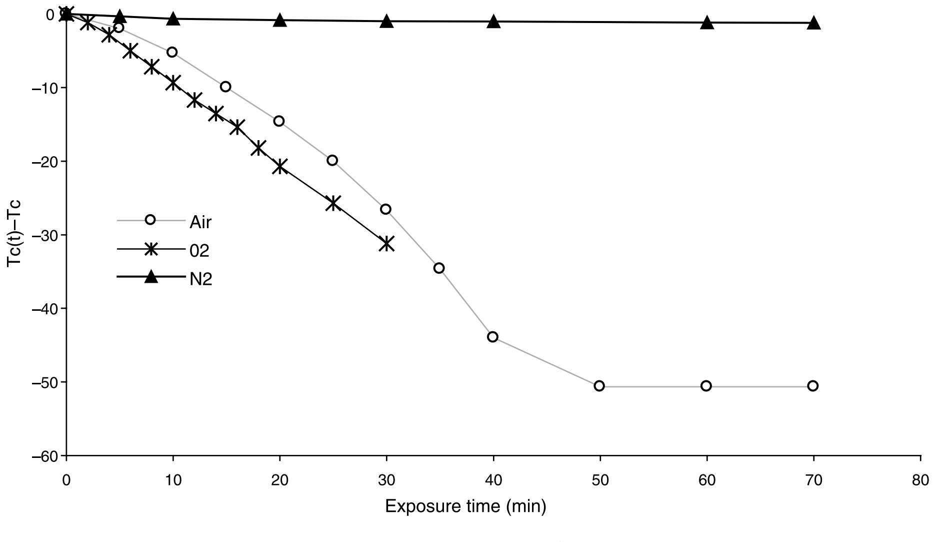

Fig. 7. Evolution of the crystallization temperature of Vestanemer irradiated at 81 mW/cm^2, 60 °C and under various atmosphere compositions (N_2, O_2 and air).

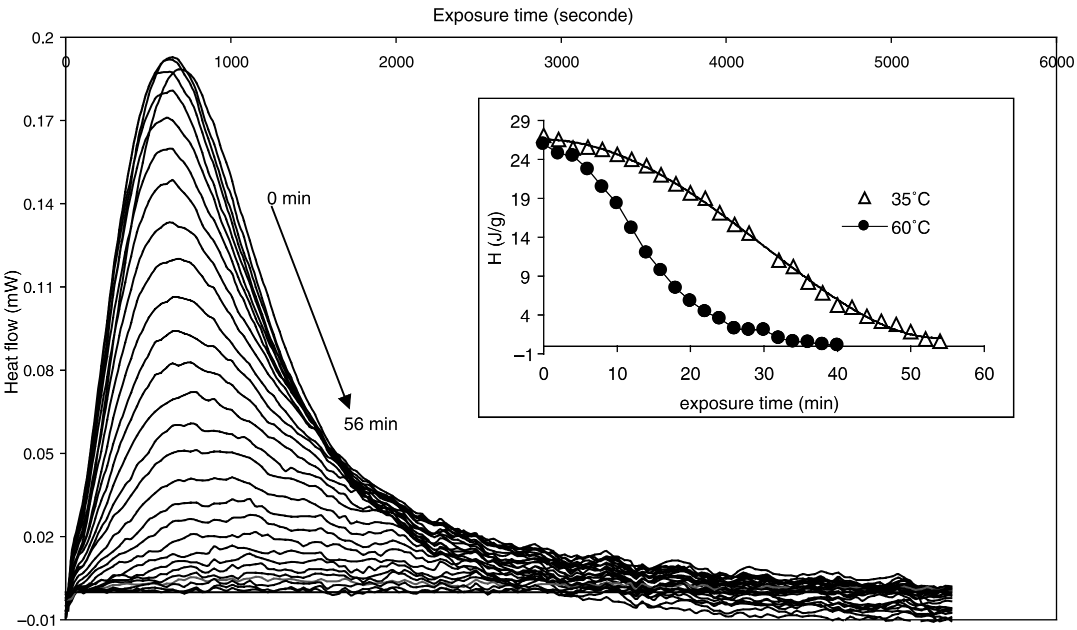

Fig. 8. Isothermal crystallization (47 °C, air) of Vestanemer irradiated at 6.5 mW/cm^2 and at 60 °C. In the insert, changes of heat of crystallization versus exposure time at 60 and 35 °C are represented.

function of exposure times at 81 mW/cm^2, 60 °C and under three atmosphere compositions. Pure nitrogen, oxygen and air were successively used. Gas was delivered with a flow rate of 30 mL/min.

As it can be pointed out, no significant modification is noticed under N_2 atmosphere. Pure oxygen seems to accelerate the decrease of the crystallization temperature of the material. These results confirm that the changes

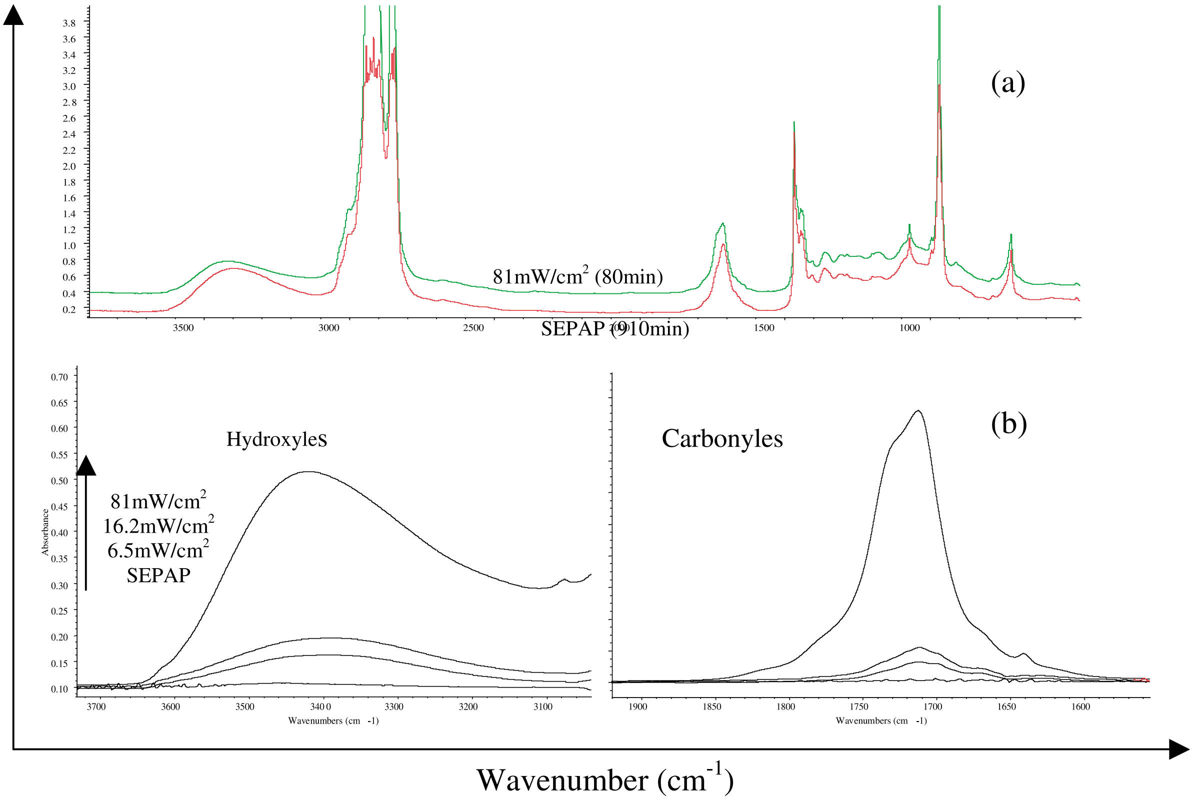

Fig. 9. IR spectra of Vestenamer irradiated at 35 °C under air atmosphere, for 910 min in SEPAP and 80 min in photo-DSC at 81 mW/cm^2 (a) and for 80 min in SEPAP device and in photo-DSC using 6.5, 16.2 and 81 mW/cm^2 as light intensity (b).

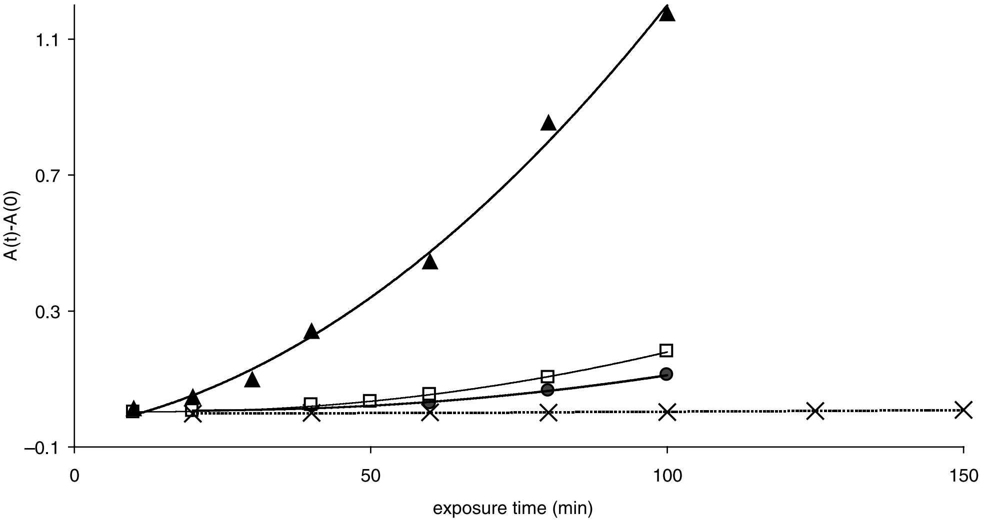

Fig. 10. IR kinetic evolution of Vestanemer in the carbonyl region (1721 cm^{-1}). Films were irradiated in SEPAP (X) and photo-DSC with light intensities of 6.5 (●), 16.2 (□) and 81 (▲) mW/cm^2. The temperature was 35 °C and atmosphere was air.

observed in the polymer crystability are attributed to an oxidative process.

3.3. Isothermal crystallization

In the last crystallization experiments, the cooling rate was taken equal to 10 °C/min. It is mentioned above that the temperature and the heat of crystallization decrease upon exposure time at given light intensity when the sample was cooled down at 10 °C/min. What about these results when the cooling rate is taken equal to zero? To answer this question, irradiations were performed at 6.5 mW/cm^2, at 35 or 60 °C and under air atmosphere. In a first experiment series, sample was maintained at 60 °C for 2 min in darkness in order to complete its melting and its thermal equilibrium. The light was on for 2 min and then off while the temperature was reduced to 47 °C at 10 °C/min. The sample was held at 47 °C for 90 min. This value (47 °C) is higher than the crystallization point of Vestanemer and lower than its melting temperature. After completion of isothermal crystallization, the sample is re-heated up to 60 °C to start a new cycle.

In the case of irradiation at 35 °C, as soon as the light was off, the sample was heated up to 60 °C in order to melt it. When the melting was complete, the temperature was down at 47 °C with a speed of 10 °C/min and the sample was maintained at this temperature for 90 min. When the isothermal crystallization was finished, the sample was cooled down to 35 °C to start a new cycle.

In Fig. 8 the results of these isothermal experiments are gathered. The exotherm areas exhibit a drastic decrease when exposure times increase. Also peak positions shift slightly to longer times indicating that the crystallization gets more and more difficult to be performed. As seen in Fig. 8, when irradiation temperature increases, the rate of decrease of the crystallinity increases too revealing that the oxidation is thermally accelerated.

3.4. Comparison with another accelerating system

SEPAP device was chosen to carry out this comparison. Vestenemer samples were irradiated under air atmosphere in SEPAP or in photo-DSC. In both cases the temperature was fixed at 35 °C. After given exposure times, IR spectra were recorded to evaluate the nature and the amount of accumulated characteristic photo-products inside the polymeric matrix.

In Fig. 9(a), two spectra are given: The first one is that of a Vestanemer film irradiated in photo-DSC at 81 mW/cm^2 and at 35 °C for 80 min using under air atmosphere and the second one is related to a film exposed in SEPAP for 910 min under the same temperature and atmosphere conditions. A strong similitude can be noticed between the two spectra. The two irradiation systems provoked the same chemical modifications of the polymeric matrix.

Fig. 9(b) represents the IR spectra in the hydroxyl and carbonyl regions of polymer films irradiated at the same exposure time, temperature and atmosphere composition either in SEPAP or in photo-DSC with light intensity ranging from 6.5 to 81 mW/cm^2. From the kinetic evolution (Fig. 10), it appeared that, whatever the light intensity, the photo-DSC system was more accelerating than the SEPAP device.

4. Discussion

4.1. Photo-DSC and accelerating conventional device

No difference in the chemical modifications of the polymeric materials and the stoichiometry of the photoproducts was observed when the polymer was irradiated either in

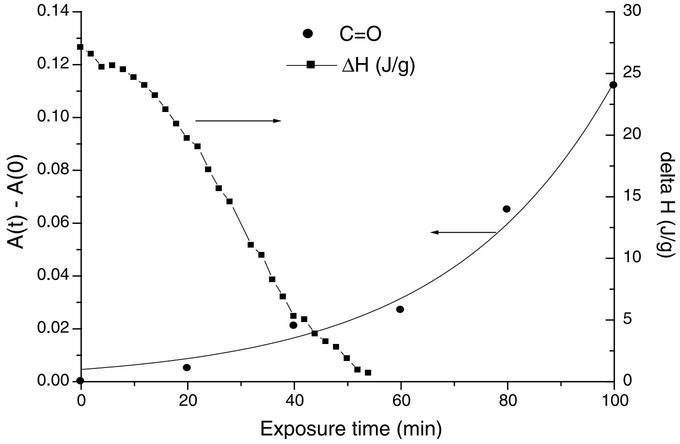

Fig. 11. Vestanemer irradiated in photo-DSC system at 35 °C, 6.5 mW/cm^2 and under air. (●) left ordinate: IR kinetic evolution of carbonyl signal (1721 cm^{-1}), (■), right ordinate: Changes in isothermal crystallinity heat (47 °C).

SEPAP or in photo-DSC. By using a higher power source at wavelengths longer than 300 nm, photo-DSC accelerated the photo-ageing considerably giving a new tool to follow and predict in situ the polymer degradation.

4.2. Aspects of exotherm of crystallization

Oxidation provoked a strong morphological alteration inside the polymeric matrix. Indeed, chain-scissions and cross linking processes led to a large modification in macromolecular mobility. In a previous work [14] describing NMR experiments, it was shown that the relaxation time (T_2) was drastically modified when the polymer was chemically cross linked. The polymeric chain mobility decreases because of the increase of cross-linking density. When the polymer was irradiated-whatever its physical state-cross linking reactions attached the macromolecules to each other. The melting process involves the crystalline part of the polymer. Consequently, when the cross-linked polymer melts, the crystalline part is in its liquid form and it soaks up the amorphous fraction constituting a tri-dimensional network. When this melting polymer cools down, the liquid part solidifies but its ability to crystallize depends on the chain mobility. This latter is reduced when the cross-linking density increases. So, when the exposure time (at a constant light intensity, Figs. 5 and 8) or the light intensity (at a given exposure time, Fig. 4) increase, the 'crystallizability' decreases. Consequently, the process of germination becomes more and more difficult and the rate of the crystal growth is slowed down. These facts are confirmed by the exotherms of crystallization that reveal a shift to low temperatures and a noticeable broadening and decreasing upon exposure.

4.3. Crystallizability and photo-products accumulation

The heat of isothermal crystallization versus exposure time and the kinetic curve of carbonyl photo-products related to Vestenamer irradiated at 35 °C in the photo-DSC system are gathered in Fig. 11. The crystallizability falls at early stages of irradiation before significant accumulation of the carbonyl. Assuming that the decreases of the polymer crystalizability is related to the network densification, Vestanemer seems predominately to undergo the cross linking reactions before a noticeable formation of oxygenated photo-products. This behavior was already mentioned in other dienic elastomers like polybutadiene [15] and ethylene–propylene–diene–monomer (EPDM) [16].

5. Conclusion

The photo-DSC system allows the combination of irradiation and analytical in situ measurements. Atmosphere, exposure time, light intensity and ageing temperature can be chosen and precisely controlled. No difference in chemical modifications of the matrix is observed when the polymer is irradiated in a classical accelerating photo-ageing device or is exposed in photo-DSC system. In the last case, depending on the light intensity, a high acceleration factor can be reached.

The ability of semi-crystalline polymer to solidify is greatly affected by the consequences of photo-ageing. Notably, cross linking, by decreasing the macromolecular chain mobility, deceases the 'crystallizability' of the polymer. Photo-DSC, by following the change of the temperature and the heat of crystallization, is a good tool to study the semi-crystalline polymer photo-ageing.

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