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short note

Formation of treeing figures during the photooxidation of polyolefins

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This paper describes a study on the surface modifications induced by the photodegradation process in polymeric materials. Several types of polyolefins (linear low density polyethylene, polypropylene) were u.v.-degraded. SEPAP 12-24 apparatus (Service d'Etude du Photovieillissement Accéléré des Polymères) was used to accelerate the degradation process. Scanning electronic microscopy of photodegraded specimen surfaces revealed the unexpected formation of treeing figures, which disappear during the storage period. The phenomenon observed on the photooxidized samples has two plausible explanations based on the presence of photoproducts in u.v.-irradiated samples: the first is that the formation of treeing figures occurs in the acceleration device; the second is that a high field is required to facilitate their formation. Some staining procedures are used to better address the findings.

(Keywords: photooxidation; polyolefins; treeing figures)

Introduction

Oxidative degradation reactions constitute the main limit to the active life span of polymers. This limiting effect may be accelerated by exposure to u.v. radiation and/or to elevated temperature. Over the past years, considerable effort has been directed towards achieving a better understanding of this degradation process. So far, research on the subject has dealt with the chemical modifications resulting from the oxidation process and monitored by i.r. or u.v. absorption changes of selected bands. These experiments, combined with chemical treatments, constitute a useful source of information on the photochemical disappearance and formation of chemical groups during the degradation process[1]. The approach used in these experiments may be extended by the use of scanning electron microscopy (SEM) in order to observe the effect of degradation on the surfaces of polymers. Such investigations are relatively straightforward since the surface of the specimen can be readily examined. In this way, the emergence of microcracks resulting from polymer photodegradation has been shown[2].

This paper deals with the surface modifications induced by u.v. light on polyolefins.

Experimental

Linear low-density polyethylene (LLDPE) samples based on butene-1 or hexene-1 comonomer provided by Exxon were used. These samples were in the form of films (100 μm thick) and contained a processing antioxidant. The samples were irradiated in a polychromatic apparatus, SEPAP 12-24 (provided by the Service d'Etude du Photovieillissement Accélèré des Polymères), which has been extensively described in previous research[3]. Briefly, it consists of a parallelepipedic reflector fitted with 4000 W medium-pressure mercury lamp in Pyrex envelopes (Mazda type MA 400). Sources were located at each corner. In the centre, the support of the sample holder was made to rotate at a constant speed. The experiment was conducted at a temperature of 60 ± 2°C. During the irradiation and storage procedures, the samples were under ambient air pressure.

The samples were removed from the irradiation chamber after increasing degradation periods. Then, they were immediately compared to the original material with respect to chemical changes in their structure and modification of their surfaces; the former effect was monitored by a Nicolet 510 spectrometer, and the latter by a Jeol JSM-35CF scanning electron microscope. Prior to any SEM observation, the degraded and undegraded surfaces of the sample were metallized in order to avoid space charge phenomena.

Results

When LLDPE is exposed to u.v. irradiation, various chemical reactions take place (for more details of these reactions, see refs 4 and 5), which result in a change in the Fourier transform i.r. (*FT* i.r.) spectrum (*Figure 1*). The changes indicate the formation of oxidation products (ketones and acids at 1715 cm^{-1}, esters at 1740 cm^{-1}, γ-lactones at 1785 cm^{-1}, hydroperoxides and alcohols at 3400 cm^{-1}, unsaturations at 909, 965 and 1640 cm^{-1}). The major band at 1715 cm^{-1} is regularly used to follow the level of oxidation during the u.v. irradiation.

Several irradiated and unirradiated samples were observed by SEM. Treeing figures unexpectedly appeared on oxidized LLDPE only (*Figure 2*); it was

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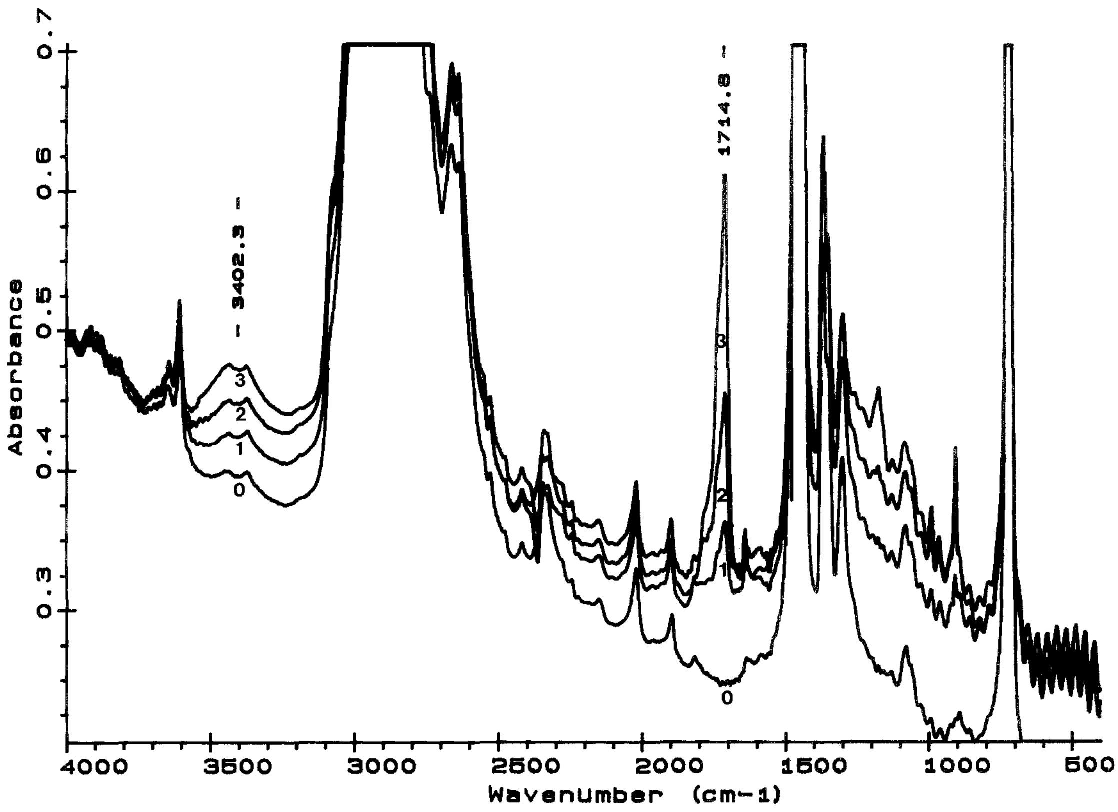

Figure 1 Evolution of the i.r. spectrum during u.v. irradiation of LLDPE in SEPAP 12-24 apparatus: 0, initial; 1, 80 h; 2, 185 h; 3, 252 h

suspected that the oxidation products formed in photodegraded LLDPE accounted for the formation of the treeing figures.

To find whether the formation of treeing figures was specific to LLDPE, the experiment was repeated with various types of polyolefins (pure polyethylene, polypropylene, copolymers provided by various companies such as Dow Chemical and BP). In these cases also, only photooxidized polyolefins displayed such patterns.

An evaluation of the degree of oxidation corresponding to the tree inception was then attempted. Several LLDPE films were u.v.-irradiated for various exposure periods. For each period, the absorbance at 1715 cm^{-1} was first estimated by *FT* i.r. Then, six to eight pieces of degraded sample (1 cm^2 surface area) were scanned with the electron microscope.

The location of the trees is random on the u.v.-irradiated samples. The results are plotted in *Figure 3*, which displays the average count number of treeing figures *versus* the absorbance at 1715 cm^{-1}. There is no correlation between the formation and the number of treeing figures on the one hand, and the oxidation level of LLDPE on the other. It is concluded that the formation of treeing figures induced by the oxidation process requires particular conditions.

The problem is further complicated by the observation that treeing figures disappear during the storage period of the u.v.-irradiated samples. The figures gradually become smaller with the storage period, as observed in electrical trees[6]. This disappearance is much faster at high temperature. For instance, complete disappearance of the treeing figures is noticed after 1 week at 80°C, and after 3 weeks at ambient temperature. In order to make the trees permanently visible, some staining procedures developed by Ashcraft and Eichhorn[7] were used. These procedures involve stains composed of methylene blue and aqueous ammonia, or methylene blue and aqueous sodium hydroxide plus a surfactant in which u.v. irradiated and unirradiated specimens were boiled with continuous stirring for times ranging from 5 to 15 min, and then rinsed in hot water and wiped with acetone. Examination of these specimens with an optical microscope revealed, on a few photooxidized samples only, pictures that looked very much like treeing figures at a disappearance stage.

Discussion

Saturated hydrocarbons, like LLDPE, slightly absorb light in the u.v. range. This absorption is ascribed to various chromophores such as impurities, defects, oxidation products, etc. During u.v. irradiation, an incoming photon is absorbed by a chromophore forming an exciton. The exciton may diffuse along the polymer chain and induce a chemical reaction leading to polymer radicals ($\mathrm{P}^{\cdot}$). In the presence of oxygen, after several steps, these macroradicals produce the oxidation products mentioned earlier.

Since treeing figures were only observed in photodegraded LLDPE, one can suspect the oxidation products generated to account for this pattern. Taking into account our irradiation conditions ($\lambda > 300$ nm, i.e. energy <4.1 eV) and the ionization potential of LLDPE (≥ 7.6 eV), we could not expect any ionization process along the molecular chain that would be capable of generating space charge. This latter is recognized as one of the causes of the electrical treeing phenomenon which occurs in polymers.

Owing to the facts that (a) no tree-inception level of

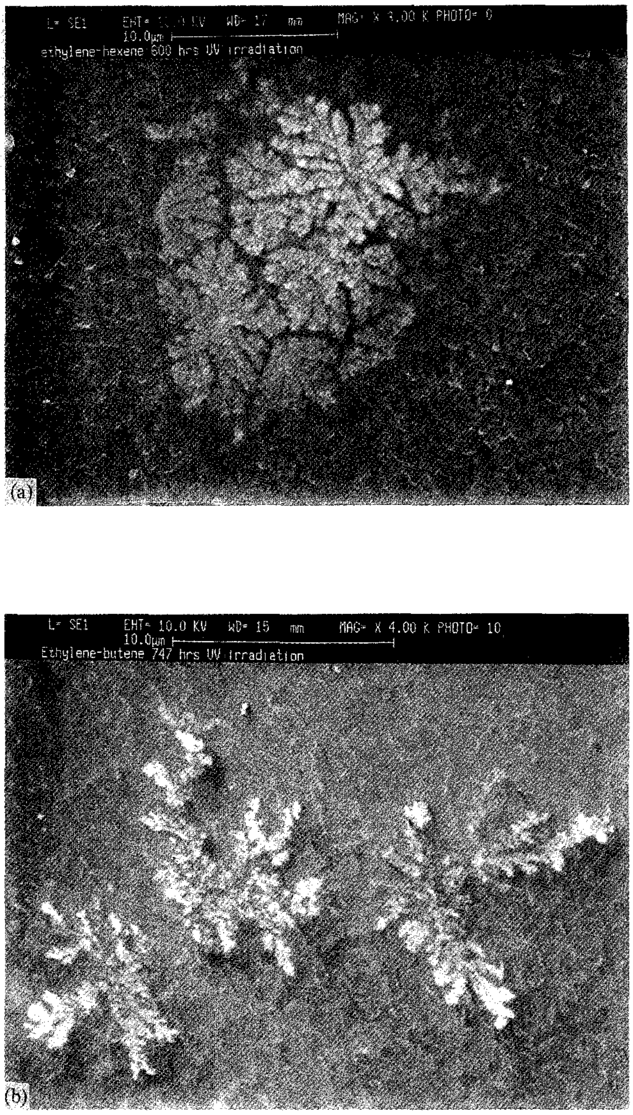

Figure 2 Treeing figures observed in LLDPE samples u.v.-irradiated in SEPAP 12-24 apparatus: (a) ethylene–hexene copolymer (600 h of u.v. exposure, equivalent to absorbance at 1715 cm^{-1} of 1.3); (b) ethylene–butene copolymer (747 h of u.v. exposure, equivalent to absorbance at 1715 cm^{-1} of 2.17)

oxidation exists, (b) no relationship exists between the level of oxidation and the number of treeing patterns, and (c) the location of the trees is random, it is strongly believed that the formation of trees may be a matter of localized concentration of the photoproducts formed during the u.v. process. This hypothesis is supported by the reported effect of u.v. light on polypropylene, which indicated the localization of oxidation[8]. Thus, in the hydrocarbon matrix, the aggregation of polar groups (acids, ketones, etc.) which constitutes dipoles is expected to generate a localized electric field. Two possibilities may be put forward: (1) the localized field may be high enough to induce a discharge leading to treeing patterns; (2) the formation of treeing patterns may take place during the metallization and/or the SEM observation, during which the samples are subjected to a high field. In that case, by analogy with the theory of Seanor[9], the equivalent circuit for a localized site of oxidation within the polymer can be represented by three capacitors: C_1, which represents the capacitance of the polymer under this site; C_2, the capacitance of the localized site of oxidation; and C_3, the capacitance surrounding the polymer, as shown in *Figure 4*. The potential distributes itself in the inverse ratio of the capacitances, and the voltage across the site of oxidation V_1 is given by:

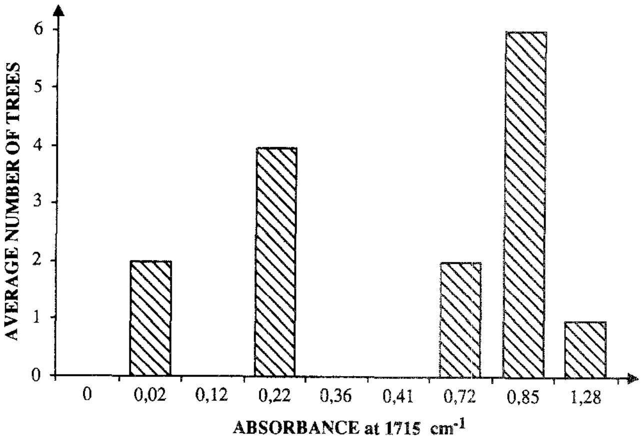

Figure 3 The average count number of treeing figures *versus* the absorbance at 1715 cm^{-1} measuring the degree of oxidation

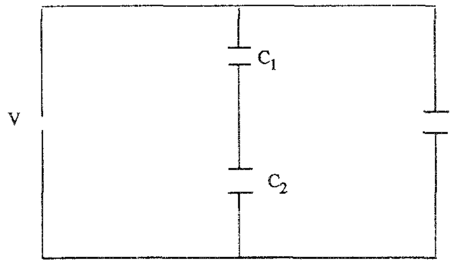

Figure 4 Equivalent circuit of a localized site of oxidation within the polymer. C_1 represents the capacitance of the polymer under this site, C_2 the capacitance of the localized site of oxidation, and C_3 the capacitance surrounding the polymer; V is the applied potential

$$V_1 = C_3V/(C_1 + C_2)$$

where V is the applied potential and $C = \epsilon/d$, with ϵ and d representing the permittivity and the distance between two parallel plate capacitors, respectively. By approximation, it has been determined that the field within the localized site of polar groups is equal to:

$$E_1 = \epsilon_3/\epsilon_1 E$$

where E is the field applied, and $\epsilon_3 > \epsilon_1$. It can be noted that the field within the localized site E_1 is higher than that within the polymer. This condition is very favourable for the occurrence of electrical discharge leading to treeing figures.

In both cases, oxidation photoproducts are directly or indirectly responsible. Additional experiments conducted to see whether the formation of treeing patterns was taking place in the irradiation chamber were unfortunately not decisive. In fact, the staining procedures used right after the u.v. irradiation do not allow us to conclude whether the treeing figures occurred in the SEPAP 12-24 conditioning chamber. The pictures observed on an etched, photodegraded specimen by optical microscopy were too uncertain to draw a final conclusion.

The disappearance of treeing figures over time can be simply explained by the rearrangement of molecular chains during the storage period. The rapidity of this disappearance at high temperature can then be easily explained by an increase in the chain mobility which facilitates this rearrangement.

Conclusion

Polyolefins subjected to u.v. radiation in conditioning chambers may display treeing figures which are probably induced by the formation of photoproducts during the process of u.v. exposure. To the best of our knowledge, it is the first time that this kind of phenomenon has been reported for u.v.-irradiated polymers ($\lambda > 300$ nm).

Two plausible mechanisms have been suggested to explain the emergence of such patterns. both are based on the localization of oxidation sites in the polymer during the photooxidation process. This idea was supported by the work of Billingham[8]. The first proposed mechanism establishes that the formation of treeing figures takes place in the conditioning chamber, while the second requires the application of a high field to facilitate their formation. Attempts using staining techniques to confirm either mechanism were unsuccessful.

Our results may shed some light on the connection of the emission of light and the degradation of polymers observed during electrical tree initiation in low-density polyethylene[10]. They may also be helpful for polymer users (e.g. power cable manufacturers) who are confronted with the problem of treeing in solid dielectrics. Further investigations are necessary to definitely elucidate the observed phenomenon.

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