

Photooxidation and Stabilization of Photooxidized Polyethylene and of Its Monopolymer Blends

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ABSTRACT: The increasing use of products from recycled polymers, or from blends with recycled polymers exposed to the outdoors, implies the need for good weathering resistance. This is particularly important when the recycled material comes, in turn, from products exposed during their lifetime to the sun. In this case the presence of C=O groups in the macromolecular chains strongly increases the photooxidative degradation kinetics of these secondary materials. In this work the change of the photooxidative degradation of blends of virgin and photooxidized polyethylene was evaluated as a function of the C=O content present in the material. As expected, the presence of the C=O groups

strongly increases the photooxidation kinetics, as revealed by the increase of the carbonyl compounds, and by the decrease of the elongation at break. It was confirmed that the increase of C=O groups is dependent on the content of the same groups, whereas this is not true for the mechanical properties. The use of UV stabilizer strongly improves the weathering resistance of these materials, which become almost insensitive to the initial amount of C=O groups. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 2244–2255, 2004

Key words: polyethylene (PE); photooxidation; stabilization; HALS; mechanical properties

INTRODUCTION

It is well known that the presence of carbonyl groups strongly increases the photooxidation of polymer materials. Through the so-called Norrish reactions, the cleavage of the C—C bonds near the carbonyl groups is easy and degradation is much faster than that of the same virgin polymer.¹ For this reason the photooxidation behavior of postconsumer photooxidized recycled plastics is very fast and stabilization is a necessary step if these secondary plastic materials are to be used outdoors.

The increasing use of recycled plastics coming from postconsumer photooxidized materials (e.g., from films for greenhouses) makes necessary a careful study of the stabilizing systems and the effect of the amount of carbonyl groups on the photooxidative degradation.

In this article the photooxidation kinetics of films with different contents of carbonyl groups was investigated. These films were made by blending the same virgin and photooxidized polyethylene, the so-called monopolymer blends.^{2–6} The presence of an antioxidant and of a new photoreactive light stabilizer also was considered.

EXPERIMENTAL

The polymer used in this work was a low-density polyethylene (FC30, produced and kindly supplied by Polimeri Europa, Italy). Melt flow index and carbonyl group amounts are reported in Table I. The polyethylene was used both as received (PE) and after being photooxidized for 96 h (PEph) as reported in the following. Melt flow index and the content of carbonyl groups of the photooxidized polymer are reported in the same Table I.

VP Sanduvor PR-31 (PR31), produced and kindly supplied by Clariant (France), was used as the stabilizing system. PR31 is a photoreactive light stabilizer (propanedioic acid [(4-methoxyphenyl)-methylene]-bis-(1,2,2,6,6-pentamethyl-4-piperidiny) ester) able to act as both a UV absorber and a hindered amine light stabilizer. Sandostab P-EPQ (P-EPQ), produced and kindly supplied by Clariant, is a secondary antioxidant, tetrakis(2,4-di-*tert*-butylphenyl)[1,1-biphenyl]-4,4'-diylbisphosphonite. The two stabilizers were added at a level of 1000 ppm.

Blends of virgin and photooxidized polyethylene were prepared, in different compositions, by using a Brabender single-screw extruder (D = 19 mm, L/D = 25) attached to a Brabender Plasticorder PLE 651 and equipped with a ribbon head. The thermal profile was 120/160/170/180°C and the screw speed was 60 rpm. The thickness of the extruded film was about 180 μm. The two pure materials were also extruded under the same processing conditions.

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TABLE I
Main Characteristics of the Virgin and Photooxidized Pure Polyethylene

Sample	MFI	Carbonyl groups
PE	0.26	0.093
PEph	0.30	1.93

All the films were photooxidized in a Q.U.V. Accelerated Weathering Tester, manufactured by the Q-Panel Company (Cleveland, Ohio). Photooxidation was carried out using 8 UVB fluorescent lamps. The cycle adopted was 8 h of ultraviolet irradiation at $T = 65^\circ\text{C}$ and 4 h without irradiation at $T = 55^\circ\text{C}$.

Infrared spectra of the polymers were recorded on a Perkin-Elmer FTIR Spectrum One spectrometer (Per-

kin Elmer Cetus Instruments, Norwalk, CT). The carbonyl index was evaluated as the ratio between the absorbances at 1713 and 1896 cm^{-1} . Because it is known that the broad absorption $\text{C}=\text{O}$ band can be resolved into six overlapping peaks,⁷ associated with different carbonyl compounds, the area between 1650 and 1840 cm^{-1} was measured to evaluate the total amount of $\text{C}=\text{O}$ groups and not only the carbonyl groups.

Gel content was evaluated by Soxhlet extraction using *p*-xylene as solvent. Approximately 0.3 g of any sample was refluxed in *p*-xylene close to its boiling point. Extraction time was about 48 h.

The heat of fusion of the materials was evaluated by differential scanning calorimetry (DSC), using a Perkin-Elmer DSC7 at a scanning rate of $20^\circ\text{C}/\text{min}$.

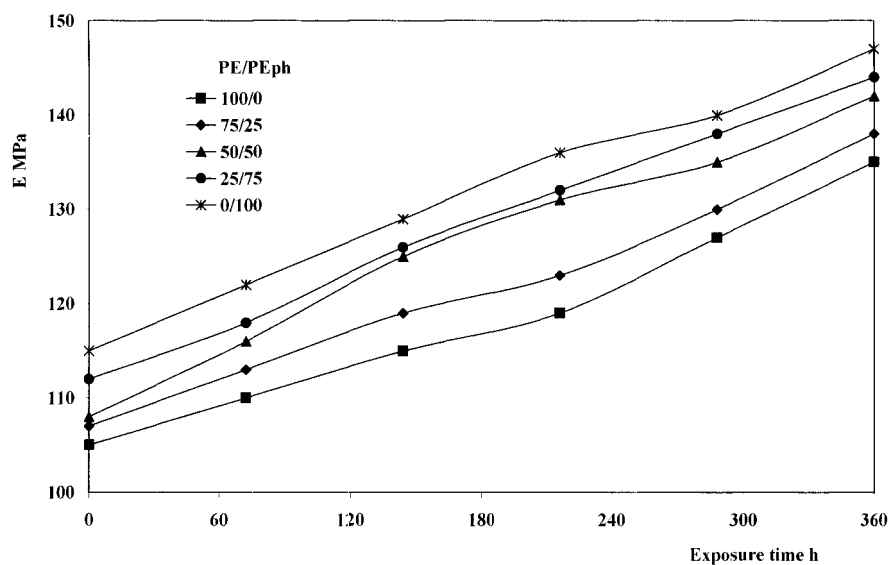


Figure 1 Elastic modulus of the two pure components and of all the blends as a function of exposure time.

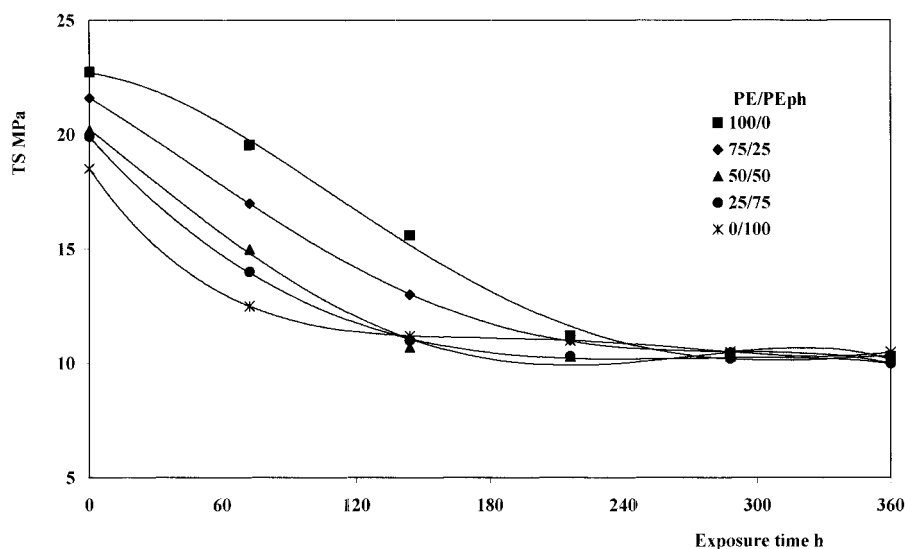


Figure 2 Tensile strength of the two pure components and of all the blends as a function of exposure time.

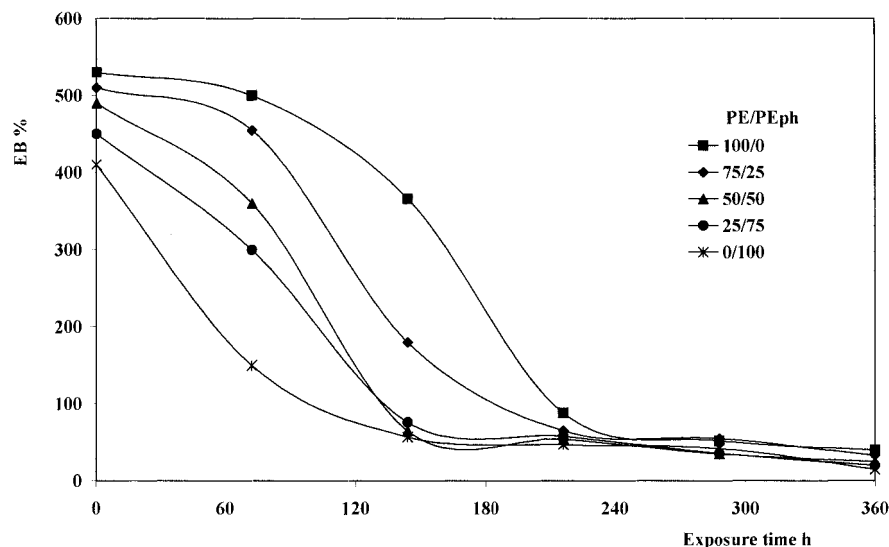


Figure 3 Elongation at break of the two pure components and of all the blends as a function of exposure time.

Mechanical properties of all the investigated materials were measured using an Instron machine model 4443 (Instron, Canton, MA) according to ASTM D882 on specimens cut from the extruded ribbons.

RESULTS AND DISCUSSION

The mechanical properties of the two pure materials and of all the blends as a function of weathering time are reported in Figures 1–3. The elastic modulus E (Fig. 1) increases with exposure time, whereas the tensile strength (TS; Fig. 2) and, in particular, the elongation at break (EB; Fig. 3) decrease. The increase of the modulus, about 25% for all the samples after 360 h of exposure, was previously explained^{8–10} considering the increase of crystallinity attributed to the decrease of the molecular weight. Indeed, the decrease of molecular weight induces a growth of crystallinity, as demonstrated by the heat of fusion of the virgin material and of the same photooxidized sample (Table II), which increases with the photooxidation time. Moreover, the formation of crosslinking can also be considered to be responsible for the increase of the elastic modulus. Moreover, extraction tests carried out on unexposed and photooxidized samples of unstabilized and stabilized materials (see Table II) have shown the presence of gel fractions increasing with the exposure time and much lower in the stabilized samples at the same photooxidation time. In fact, the decrease of molecular weight seems small, considering the small increase of the melt flow index. It is worth noting, however, that the presence of a significant content of crosslinked molecules (gel content ~ 6.6%) counterbalances the decrease of viscosity attributed to the breaking of the macromolecules. Moreover, the heat of fusion reflects a large increase of

crystallinity because it pertains only to the non-crosslinked fraction of polymer that decreases with the exposure time.

The elongation at break drastically decreases and the material becomes brittle. The exposure time at which the elongation at break becomes brittle changes and, in particular, decreases with the amount of the photooxidized component. After about 150 h the PEph-rich blends become brittle, whereas about 250 h is needed for the pure nonphotooxidized material to reach this stage. The decrease of tensile strength and elongation at break can be correlated with the decrease of molecular weight and with the formation of surface defects in the sample^{11,12} caused by the UV radiation that propagates along the specimen, thus inducing a premature rupture. Moreover, increases in the crystallinity and crosslinked fraction tend to decrease the elongation at break.

With respect to the influence of the presence of photooxidized material in the blend, the higher the content of recycled material, the faster the change of

TABLE II
Heat of Fusion and Gel Content of Some Stabilized and Unstabilized Samples

Sample	Heat of fusion (J g ⁻¹)	Gel content (%)
PE	83.9	0
PEph	87.6	6.6
PE, 360 h	125.1	17.8
PEph, 360 h	131.6	22.4
PE + PR31 + P-EPQ	83.7	0
PEph + PR31 + P-EPQ	86.4	5.2
PE + PR31 + P-EPQ, 1440 h	103.0	15.4
PEph + PR31 + P-EPQ, 1440 h	119.5	19.5

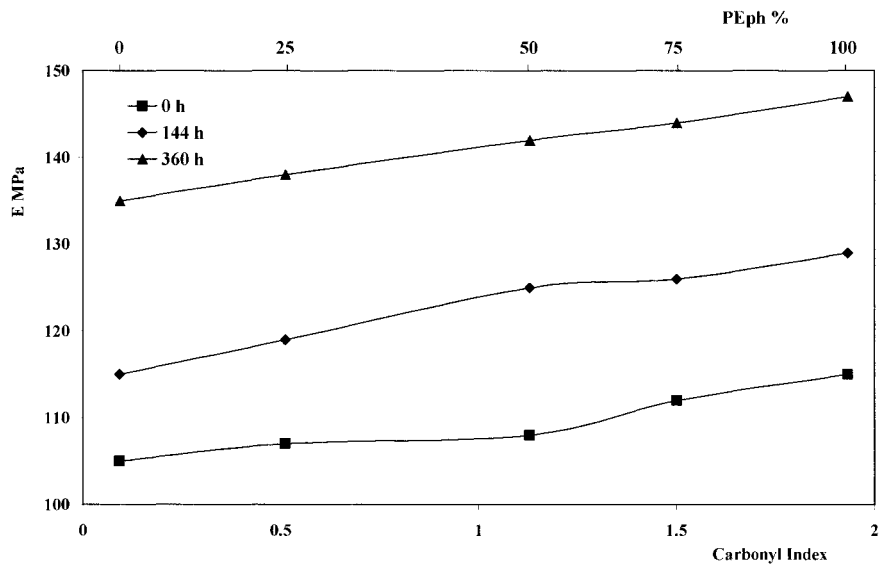


Figure 4 Elastic modulus at three fixed exposure times as a function of the content of photooxidized component and of the content of C=O groups.

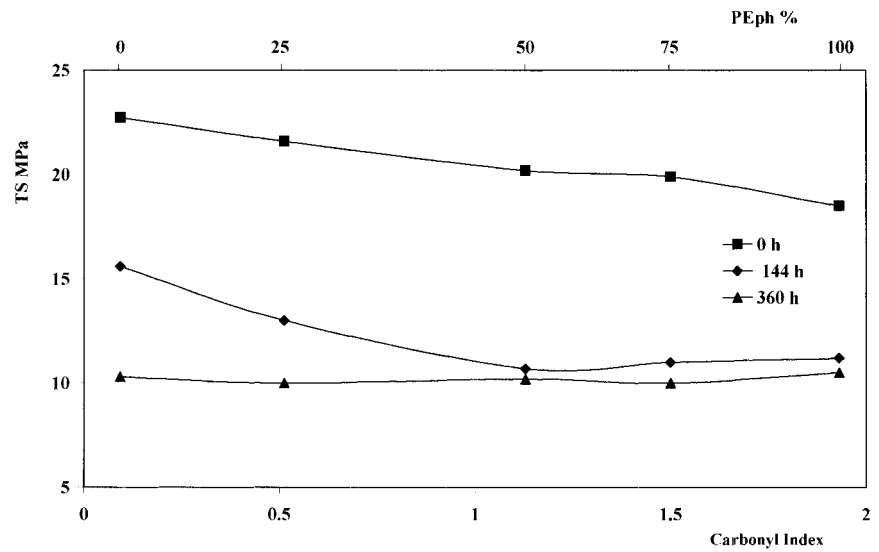


Figure 5 Tensile strength at three fixed exposure times as a function of the content of photooxidized component and of the content of C=O groups.

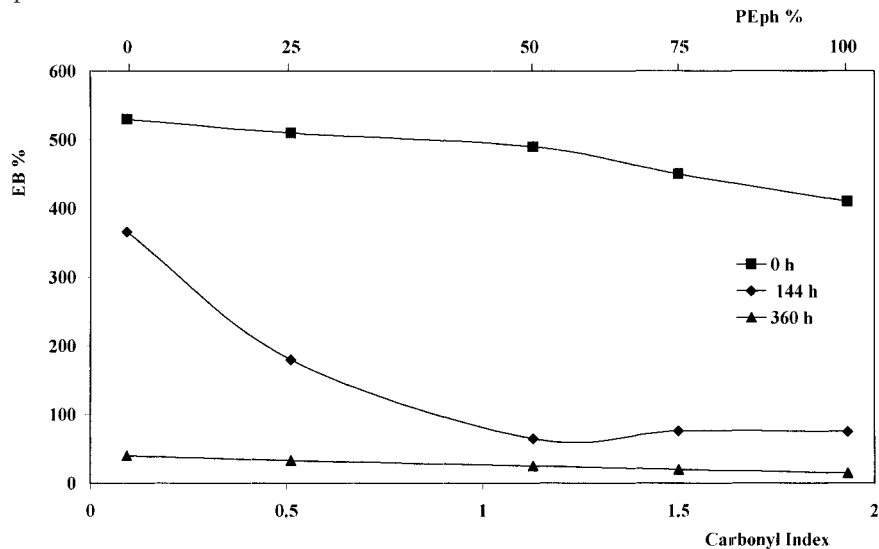


Figure 6 Elongation at break at three fixed exposure times as a function of the content of photooxidized component and of the content of C=O groups.

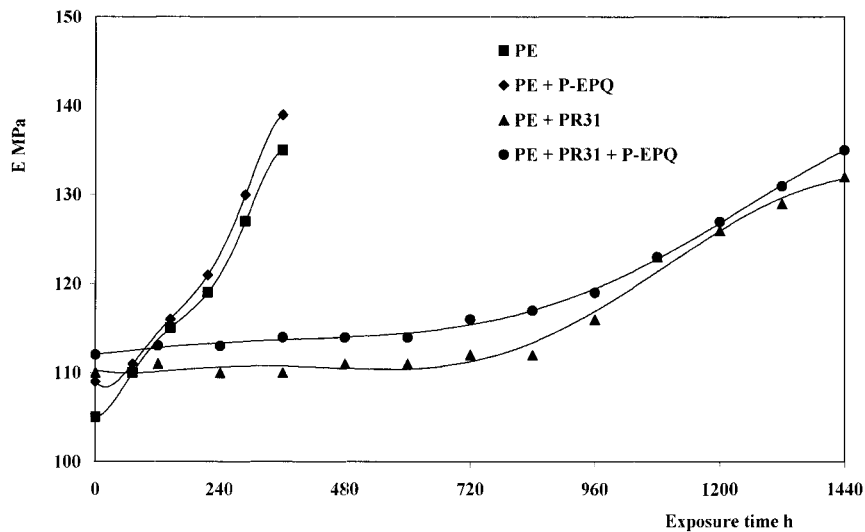


Figure 7 Elastic modulus of unstabilized and stabilized PE samples as a function of exposure time.

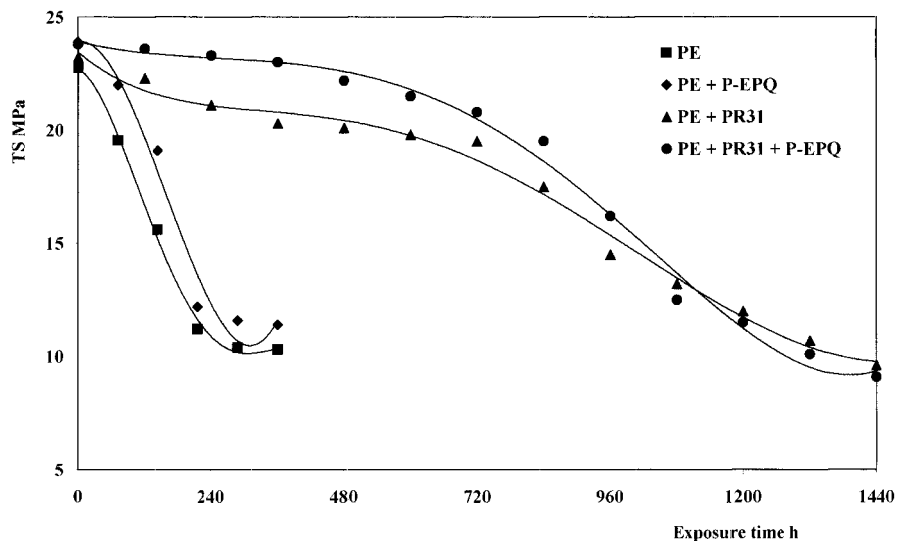


Figure 8 Tensile strength of unstabilized and stabilized PE samples as a function of exposure time.

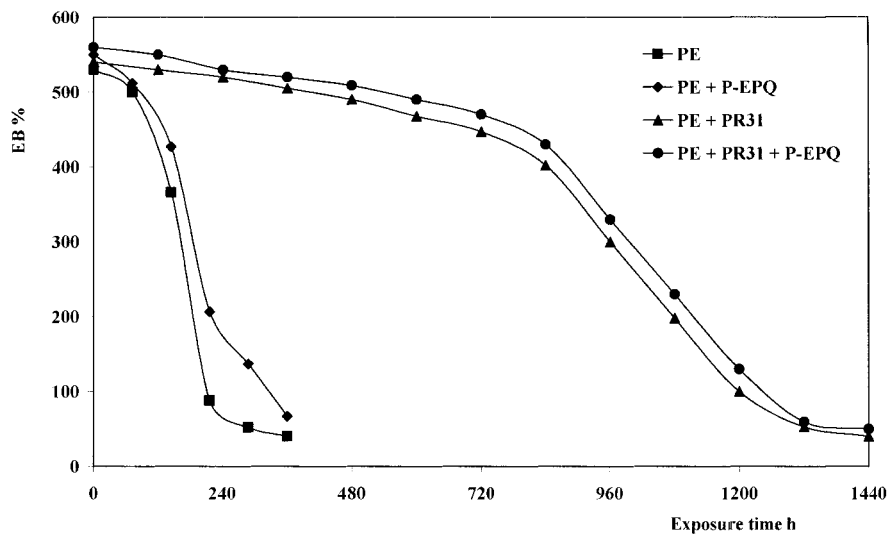


Figure 9 Elongation at break of unstabilized and stabilized PE samples as a function of exposure time.

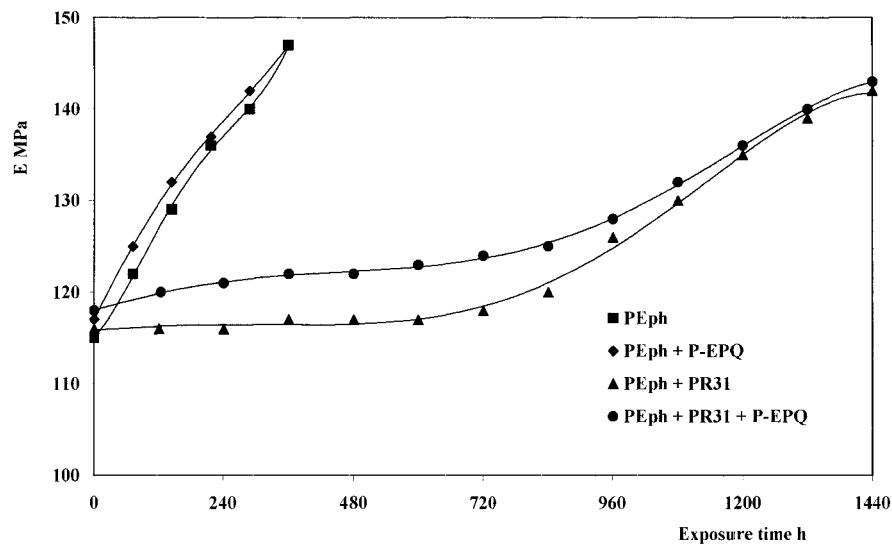


Figure 10 Elastic modulus of unstabilized and stabilized PEph samples as a function of exposure time.

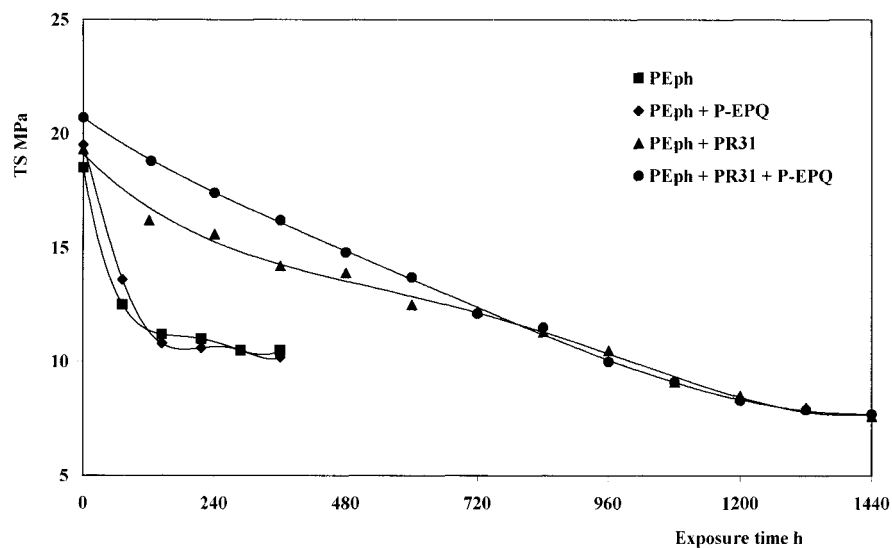


Figure 11 Tensile strength of unstabilized and stabilized PEph samples as a function of exposure time.

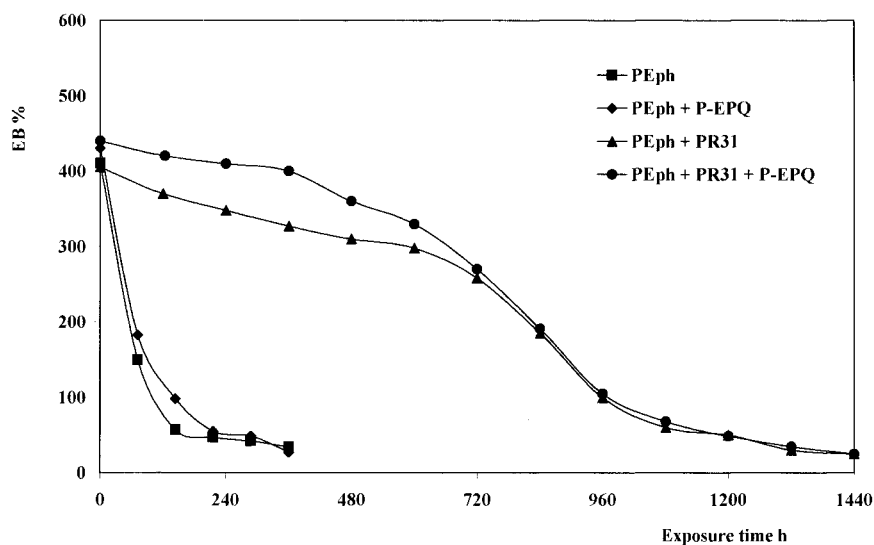


Figure 12 Elongation at break of unstabilized and stabilized PEph samples as a function of exposure time.

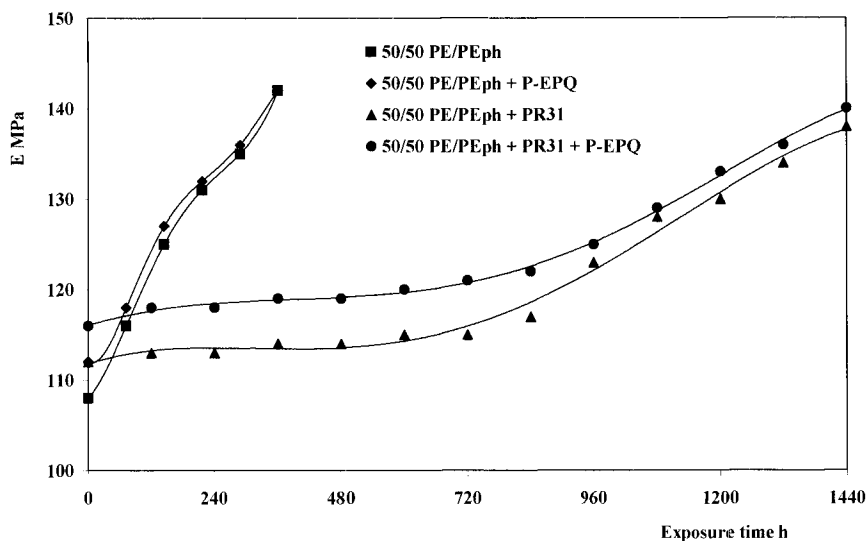


Figure 13 Elastic modulus of unstabilized and stabilized 50/50 PE/PEph samples as a function of exposure time.

the mechanical properties. The dramatically different behavior in the photooxidative degradation clearly depends on the amount of the photooxidized polymer and on the content of initial C=O groups.

To better understand the effect of the composition and of the C=O groups, the previously reported mechanical properties have been plotted (Figs. 4–6) as a function of the content of the photooxidized component, and then of the content of C=O groups, at three fixed photooxidation times. The values of the mechanical properties, and particularly of the rupture characteristics, for the unexposed samples are only slightly dependent on the composition and then on the amount of carbonyl groups. The same comments can be made for the specimens exposed for a long time. On the contrary, a dramatic dependency on the composi-

tion is observed for intermediate exposure times. Although it is well known that the change of mechanical properties does not depend only on the amount of the carbonyl groups, these results can be interpreted considering that, at the beginning of the exposure, the photooxidative kinetics are faster as the content of carbonyl groups is greater. With increasing photooxidation time, all the specimens presented a considerable content of C=O groups and then the degradation kinetics became similar.

The effect of the antioxidant, of the light stabilizer, and of the stabilizing system with the two components was tested on all the samples. For the sake of clarity and simplicity only the results relative to the two pure materials and to the 50/50 blend are reported here in Figures 7–15. The main features observed for the un-

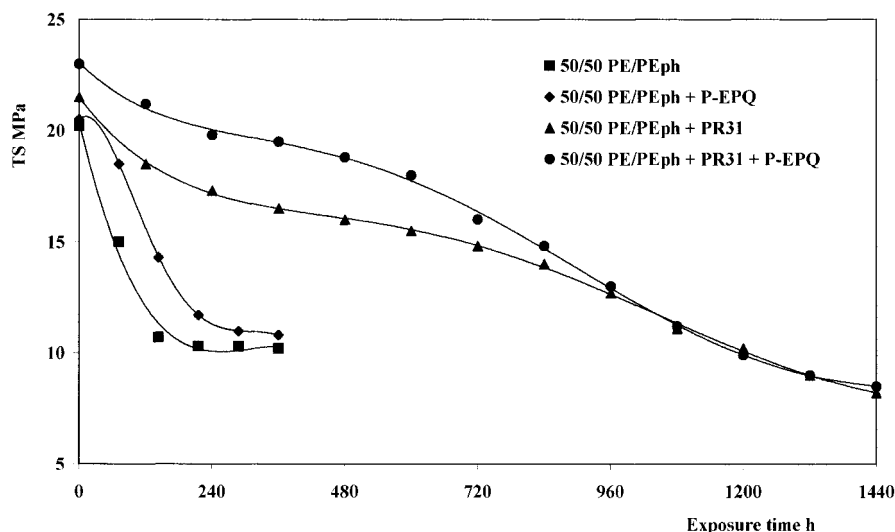


Figure 14 Tensile strength of unstabilized and stabilized 50/50 PE/PEph samples as a function of exposure time.

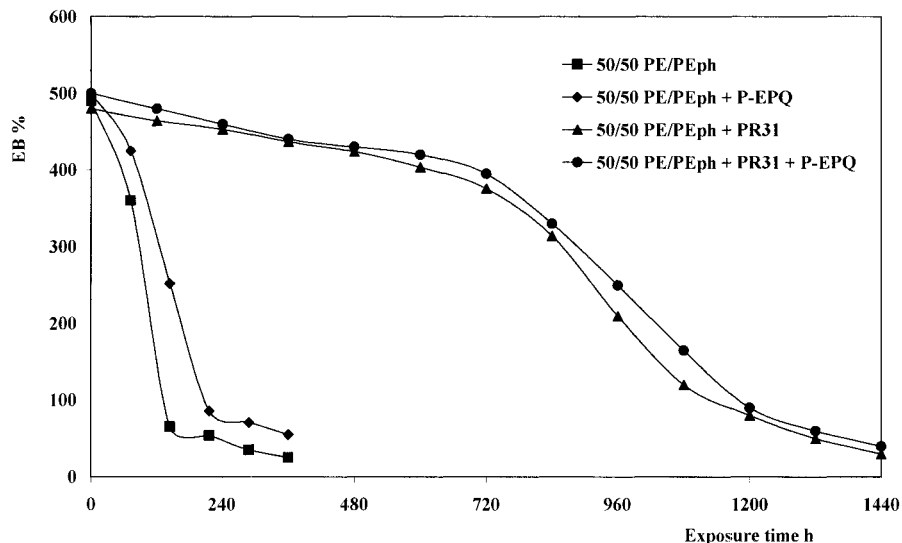


Figure 15 Elongation at break of unstabilized and stabilized 50/50 PE/ph samples as a function of exposure time.

stabilized samples are maintained for the stabilized materials: in particular, the modulus increases with exposure time, whereas the breaking properties decrease. However, the photooxidative kinetics are substantially changed.

Unstabilized materials and the samples stabilized with the antioxidant show about the same behavior and indeed only a very small improvement of the photooxidative resistance was observed when the antioxidant was added to the polymer. The presence of the light stabilizer, in contrast, dramatically improved the weathering resistance of the materials and a small synergistic effect was observed when the antioxidant was added to the light stabilizer. The addition of the antioxidant was made because, during the processing, some C=O groups can be formed as a result of the

thermomechanical treatment and the presence of these groups could accelerate the photooxidation kinetics. However, the limited formation of carbonyl groups during processing implies that the presence of the antioxidant has an effect on the photooxidation.

The virgin material becomes brittle only after more than 1300 h in the presence of PR31, whereas the photooxidized sample reaches this limit after about 1200 h. As for the blend, the time during which the material becomes brittle is intermediate. The life of all the samples increases by about four times. Similar comments can be made for the tensile strength, but the decay is slighter, whereas the increase of elastic modulus is severely delayed. To better understand the effect of the three stabilizer systems, the dimensionless elongation at break is plotted in Figures 16–18 for the

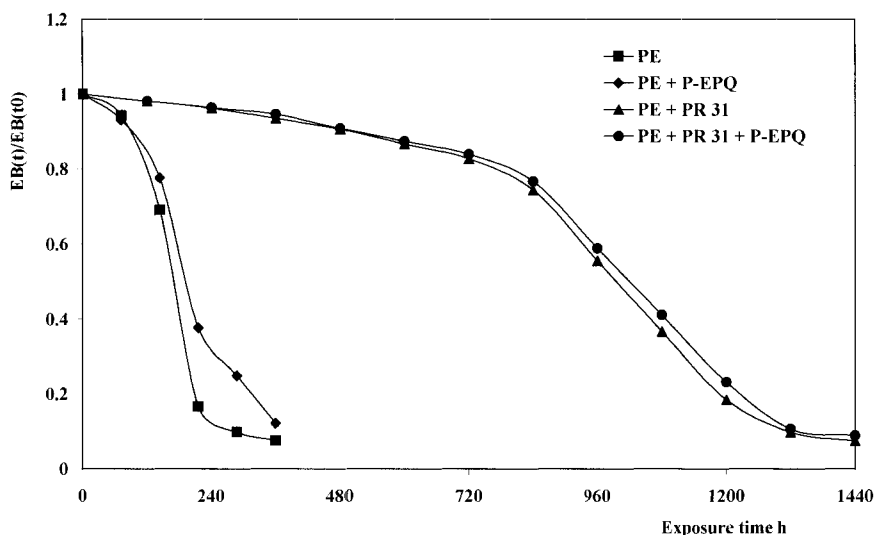


Figure 16 Dimensionless elongation at break of unstabilized and stabilized PE samples as a function of exposure time.

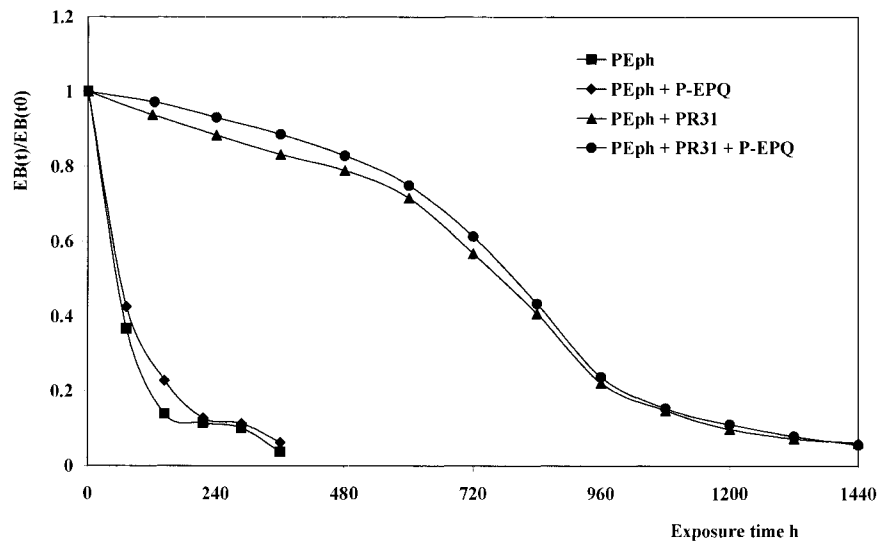


Figure 17 Dimensionless elongation at break of unstabilized and stabilized PEph samples as a function of exposure time.

three unstabilized systems, and for the same materials stabilized with the two additives. The dimensionless values were obtained by dividing the value of the elongation at break at a given time by the value of the unexposed sample. Elongation at break is the mechanical property sensitive to photooxidative degradation because it is highly dependent on both molecular structure and morphology and on the possible surface defects. The significant effect of the light stabilizer is evident: the elongation at break–exposure time curves of the samples stabilized with PR31 and with PR31 and the antioxidant are much greater than those of the unstabilized polymer and of the samples with the antioxidant.

The shifting toward longer times of the beginning of the decay of the elongation at break is the main feature that can be observed from the previous graphs.

The stabilization, as previously stated, strongly enhances the lifetime of these materials. In Table III the time at which the elongation at break becomes one half of the initial values ($t_{0.5}$) and the time at which the elongation at break becomes 50% (t_{50}) are reported for all the specimens. Two features are evident from these curves and from the data of Table III: the presence of UV stabilizer gives rise to a dramatic shift of the exposure time at which damage starts and the stabilization becomes more effective with increasing the amount of photooxidized components. Indeed, al-

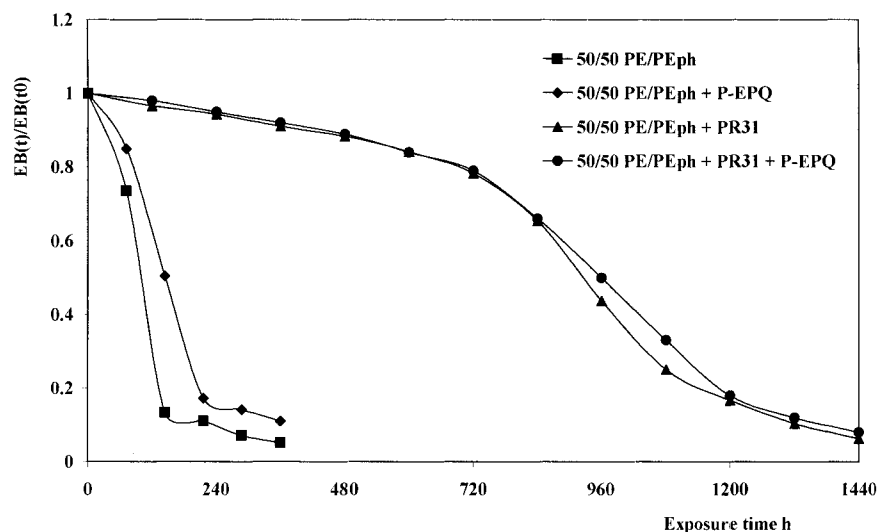


Figure 18 Dimensionless elongation at break of unstabilized and stabilized 50/50 PE/PEph samples as a function of exposure time.

TABLE III
Time at Which the Elongation at Break Becomes One Half of the Initial Value ($t_{0.5}$)
and Time at Which the Elongation at Break Becomes 50% (t_{50})

PE/PEph	P-EPQ	PR31	PR31 + P-EPQ
Elongation at break ($t_{0.5}$ h)			
100/0	170	190	1000
75/25	123	145	960
50/50	100	145	930
25/75	96	105	870
0/100	52	60	780
Elongation at break (t_{50} h)			
100/0	300	360	1350
75/25	280	330	1320
50/50	230	300	1300
25/75	210	280	1250
0/100	150	200	1200

though for the unstabilized materials the differences for $t_{0.5}$ and t_{50} are very large with increasing the contents of C=O groups, this difference diminishes in the presence of a UV stabilizer. As discussed earlier, the presence of the antioxidant is not particularly effective because, under the adopted processing conditions, almost no degradation occurs and then the amount of the C=O groups, that are responsible for further degradation during photooxidation, does not increase.

The efficiency of PR31 seems attributable to its ability to act as both UV absorber (absorption between 250 and 350 nm) and a hindered amine light stabilizer. Moreover, it has been hypothesized that the molecules can become chemically bound to the polymer matrix, thus avoiding any loss and migration of additive.¹³

The increase of carbonyl index is, with the decrease of the molecular weight, the most important effect of the photooxidation. Figures 19 and 20 report, as examples, the growth of the carbonyl index as a function of the exposure time for the unstabilized and stabi-

lized materials. In previous work¹⁴ the carbonyl index–photooxidation time curves were superimposed by shifting the same curves toward higher times with increasing the initial content of the C=O groups. By using the same shift factors used for the superposition of the curves relative to the unstabilized material, the carbonyl index–exposure time curves of the stabilized polymer can be superimposed very well, generating a generalized curve, as shown in Figure 21 for the samples stabilized with the two additives. Similar results were obtained for the other stabilized materials. The existence of this shift has been explained considering that the presence of C=O groups reduces the induction time of the photooxidation: this interpretation also seems to hold for the stabilized materials. In contrast, the same superposition does not hold for the mechanical properties (curves not reported here) because these properties depend on many other parameters and certainly not only on the content of carbonyl groups.

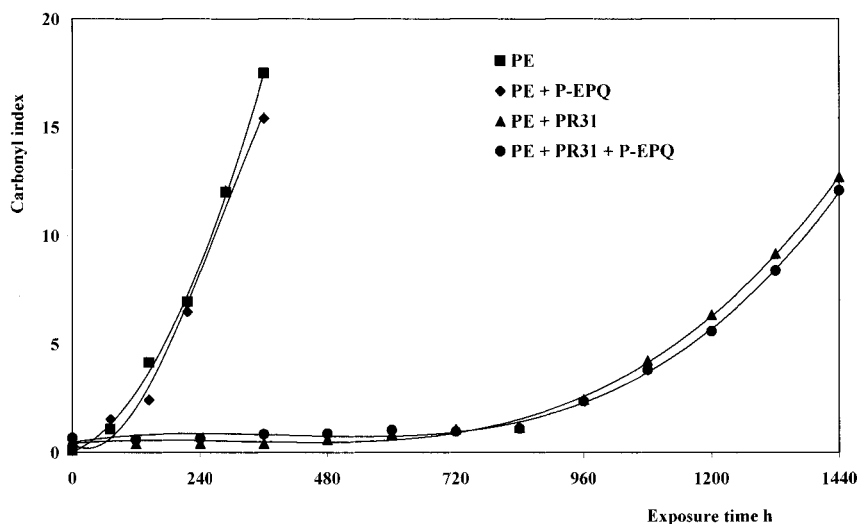


Figure 19 Carbonyl index as a function of exposure time for the unstabilized and stabilized PE samples.

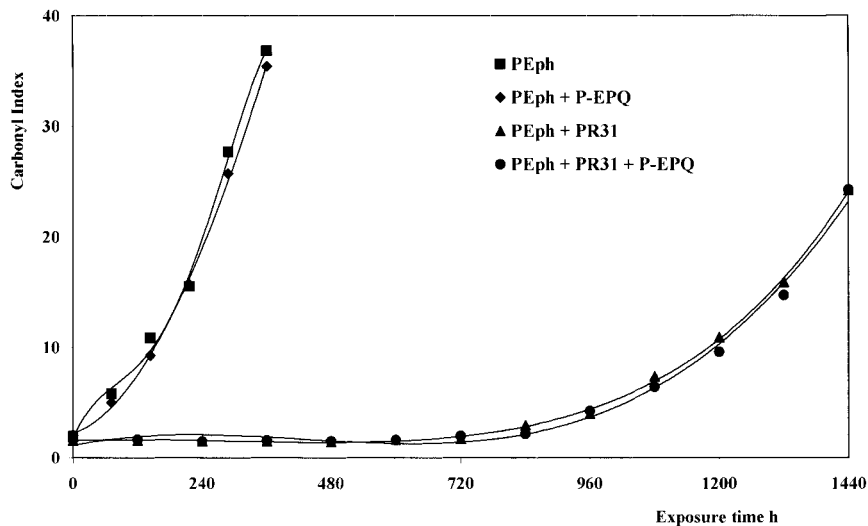


Figure 20 Carbonyl index as a function of exposure time for the unstabilized and stabilized PEph samples.

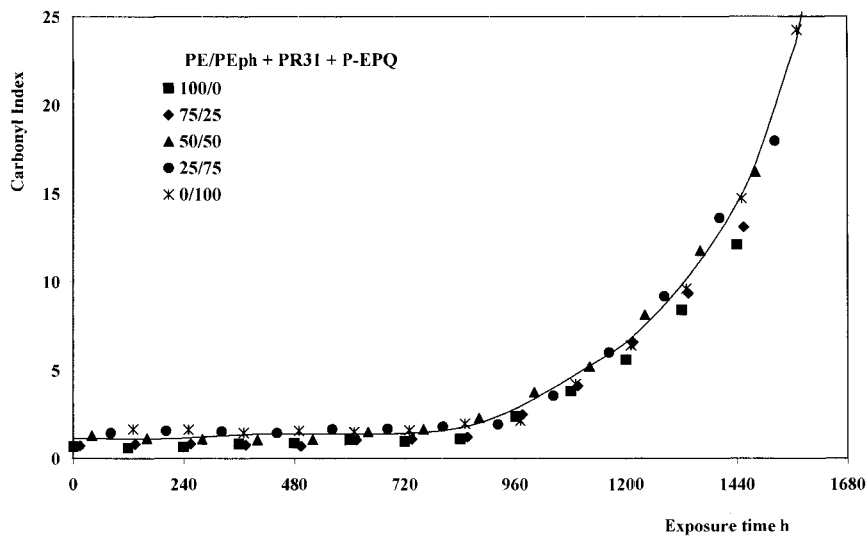


Figure 21 Generalized curve of the carbonyl index for a stabilized system.

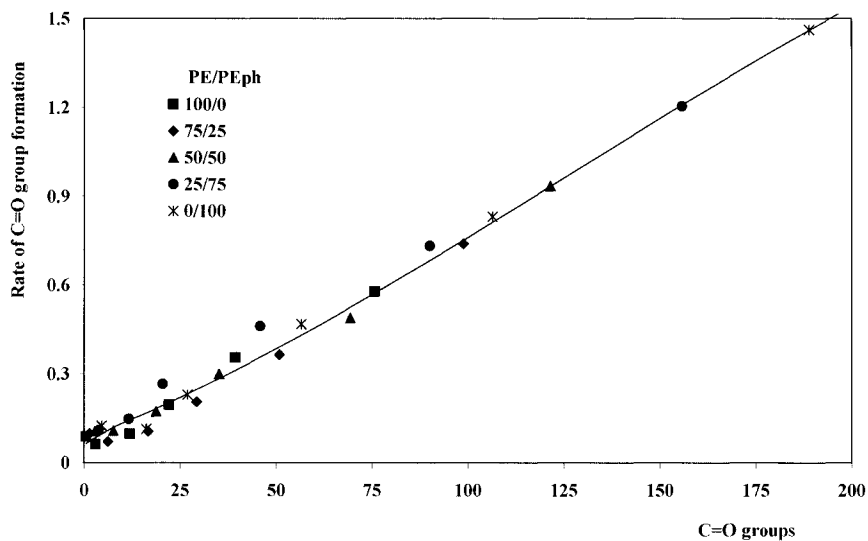


Figure 22 Rate of C=O group formation as a function of the content of C=O groups for the unstabilized PE samples.

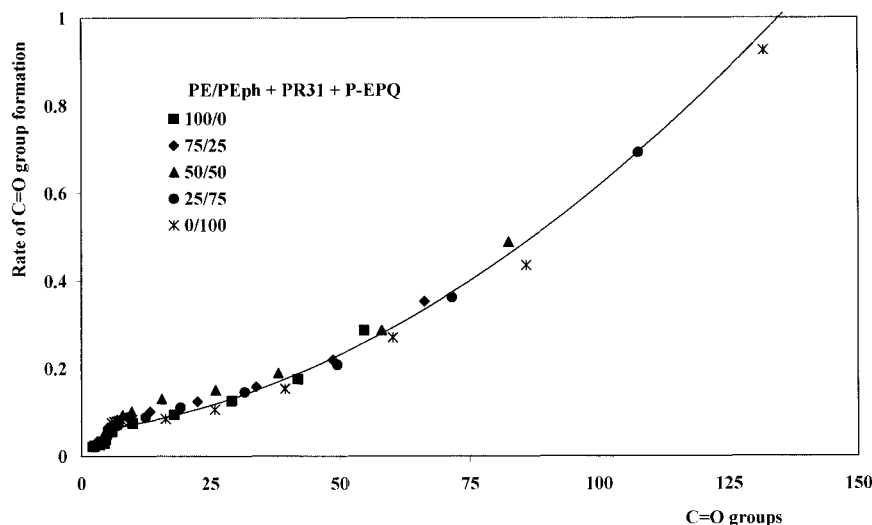


Figure 23 Rate of C=O group formation as a function of the content of C=O groups for the PR31/P-EPQ stabilized PE samples.

The influence of the initial content of carbonyl groups on photooxidation kinetics is qualitatively clear. To propose a more quantitative evaluation of this influence, the rate of C=O groups formation was calculated as the slope at given times of the C=O groups–exposure time curves. The results were plotted for the unstabilized materials and for those stabilized with the two additives against the total C=O group content (area between 1650 and 1840 cm^{-1}) at the time at which the slope was measured (see Figs. 22 and 23, respectively). Similar plots were drawn for the other two materials and are not reported here. Rates of C=O group formation for both unstabilized and stabilized samples fall on the same curve, clearly suggesting that, under fixed photooxidation conditions, the rate of formation of these groups is dependent on the amount of these groups present in the sample.

CONCLUSIONS

The photooxidation kinetics of secondary plastic materials derived from photooxidized plastics and of their blends with the same virgin polymer is strongly accelerated because of the presence of C=O groups. It has been shown that the increase of carbonyl groups is directly correlated to the content of the same groups in the sample, whereas the deterioration of mechanical properties increases with increasing content of carbonyl groups, but cannot be directly related only to this parameter.

The presence of UV stabilizer strongly improves the oxidative stability of these materials. Moreover, the

efficiency of the UV stabilizer PR31 seems to increase with increasing the C=O groups. The presence of an antioxidant does not significantly improve the protective action, provided no thermomechanical degradation occurs during the processing. Indeed, only in presence of C=O groups formed during processing should the photooxidation rate increase.

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