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Influence of a Sterically Hindered Amine on the Photo-oxidation of Low Density/Linear Low Density Polyethylene Blends

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ABSTRACT

Low density/linear low density polyethylene blends show a rate of degradation of the mechanical properties during photo-oxidation which increases with the content of the linear polymer. The use of a sterically hindered amine as UV stabilizer greatly improves the resistance of these blends to UV irradiation. The effectiveness of the stabilizer increases with the content of linear low density polyethylene.

INTRODUCTION

Previous work[1–3] has demonstrated the possibility of obtaining a new class of polymer blends with easy processability[1,2] and good mechanical properties[3] from low density polyethylene and linear low density polyethylene. These blends make it possible to obtain products (such as packaging, greenhouse coverings, etc.) with a significant reduction of thickness, thus overcoming the drawback of the poor processability of LLDPE on standard industrial blown film equipment.

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Previous work[4] has demonstrated, however, that linear low density polyethylene undergoes a rapid decrease in mechanical properties when it is subjected to ultraviolet irradiation. Also, of course, the blends degrade at a much higher rate than that of pure low density polyethylene. Moreover, the reduction in thickness might induce more severe photo-oxidation. It is therefore very evident that UV stabilization is extremely important for the use of these products outdoors.

In this paper, which follows a previous paper[4] on the photo-oxidation of unstabilized LDPE/LLDPE blends, the kinetics of photo-oxidation of these blends stabilized with a hindered amine has been studied by means of mechanical tests and infrared spectroscopy.

This type of UV stabilization system has been found to be extremely effective in assuring a very long lifetime for polymeric products.[5–7]

EXPERIMENTAL

Materials and sample preparation are the same as those used in the previous work.[4]

The pure polymers were a sample of linear low density polyethylene and a sample of low density polyethylene copolymerized with butene. Their main physico-chemical characteristics are reported in Table 1.[3] The two samples have about the same density and the same molecular weight and polydispersity to avoid any effect of these parameters on the photo-oxidation kinetics.

The blends were prepared by melt mixing the parents in a Brabender Plasticorder model PLE 330 equipped with a mixer head type W 50 EH. The mixing conditions were 200°C and 20 rpm for about 20 min. After this time, the torque, which was continuously recorded, was almost constant for all the blends. The pure polymers were also subjected to the same procedure.

TABLE 1

Main Properties of the Raw Material

	MFI[a]	$\rho(g/cm^3)$[b]	$Mw \times 10^{-3}$[c]	*Mw/Mn*	*g*[d]	*Ti (ppm)*	*Al (ppm)*
LDPE	2·90	0·921 5	106	4·6	0·17	<2	5
LLDPE	1·10	0·923 7	136	4·2	0·91	12	27

[a] ASTM D-1238-73 method, procedure B.

[b] ASTM D-1505-68 method.

[c] GPC in ODCB at 135°C.

[d] Branching index $g = \frac{[\eta]_b}{[\eta]_l}$ where $[\eta]_l = 4{\cdot}6 \times 10^{-3} Mw^{0{\cdot}725}$ in THN at 130°C.

The compositions investigated, ψ, contained 0, 25, 50, 75, 85, 100 wt% of LLDPE.

The hindered amine was a poly{[ethylene(2,2,6,6-tetramethyl-4-piperidyl)-imino]-hexamethylene-[(2,2,6,6-tetramethyl-4-piperidyl)-imino]} commercially known as Spinuvex A36 produced and kindly supplied by Montefluos (Italy). The concentration used in the blends was 0·1% wt/wt. A few tests were carried out with one half of this concentration but only with the homopolymers.

Sheets of these blends and of the pure polymers, about 140 μm thick, were prepared by compression moulding at 200°C under a pressure of about 100 MPa in a Carver laboratory press.

The photo-oxidation was carried out, for various lengths of time, by exposing the specimens to a Xenon lamp (Osram XBO 150 W/1) without filter, at a distance of about 30 cm. The dose rate was about 120 W/m^2 as measured by means of a thermopyle Eppley model G3. The test temperature was 60°C in order to reduce the irradiation time.

Stress–strain tests were carried out using an Instron Tensile Testing machine model 1115. The drawing velocity was 20 cm/min and the gauge length was about 3 cm. All the results are averages of at least ten measurements.

IR absorption spectra were obtained by means of a Perkin–Elmer infrared spectrometer model 1420 linked to a Data Station Perkin–Elmer model 3600. The carbonyl index, used as an index of the degree of photo-oxidation, has been evaluated as the ratio between the absorbance at 1715 and at 1895 Å, which is indicative of the CH groups, to avoid the influence of variations in the thickness.[8] The greatest difference in thickness was less than 10%; such a difference practically does not influence the oxygen diffusion rate into the polymer and consequently the oxidation rate.

The catalyst residues (Ti and Al) were determined by atomic absorbance in flame using a Perkin–Elmer instrument model 5000.

RESULTS AND DISCUSSION

The influence of the UV stabilizer is obvious in Fig. 1, where the elongation at break versus the irradiation time is plotted for the two homopolymers. As shown in the previous paper,[3] the elongation at break decreases rapidly, after a short induction time, especially for the linear low density polyethylene. Indeed, although the initial elongation at break is larger for the LLDPE sample, after 100 h of ultraviolet irradiation, ε for the low density polyethylene is slightly larger. On the contrary, for the stabilized samples, the photo-oxidation of the linear low density polyethylene is much

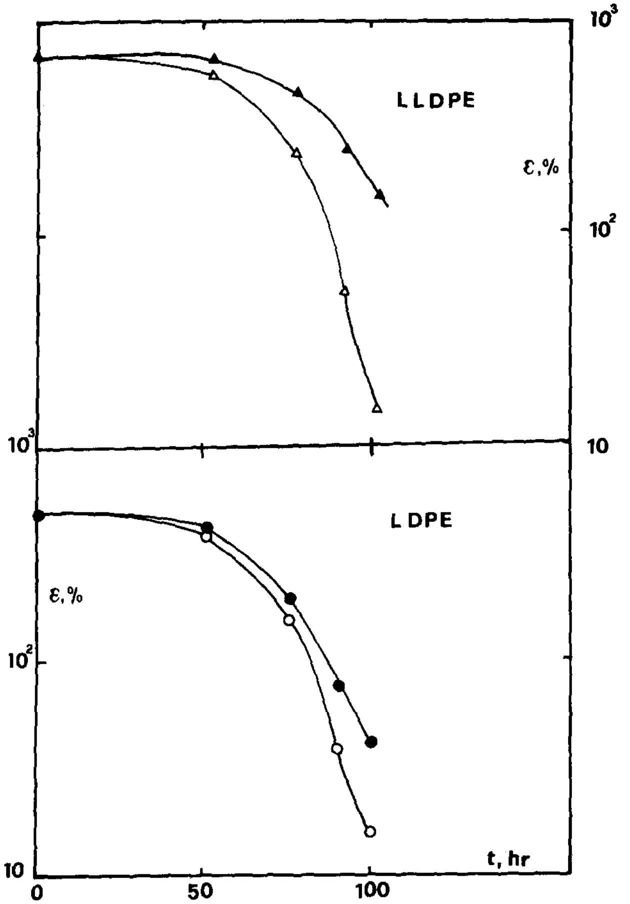

Fig. 1. Elongation at break as a function of exposure time for the two homopolymers. Open points refer to the unstabilized films; closed points to the stabilized films.

slower and, again, after 100 h of exposure, the elongation at break of this sample is more than three times that for the LDPE sample. Thus, this stabilizing system is more effective when it is used with the linear low density polyethylene.

Figure 2 reports elongation at break data for all the samples at fixed irradiation times. At low irradiation times a small but significant influence of the stabilizer is very obvious only for LLDPE-rich blends and for pure LLDPE. On increasing the exposure times, the effect of the hindered amine is obvious for all the samples, but is again larger for the LLDPE and LLDPE rich blends.

Similar comments can be made as far as the carbonyl index is concerned, Fig. 3. Contrary to the elongation at break, the carbonyl index of the unstabilized samples is almost independent of the composition. For the

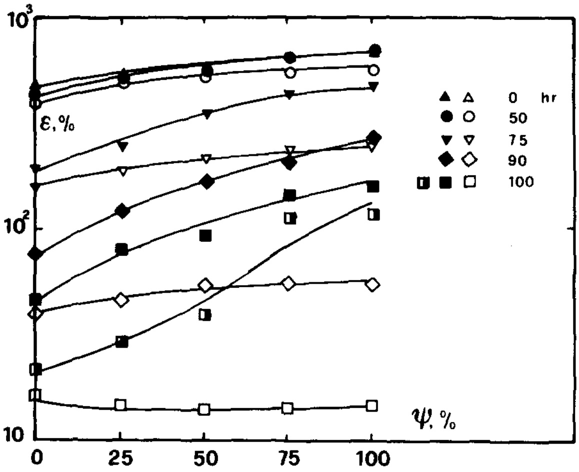

Fig. 2. Elongation at break versus linear low density polyethylene content at a fixed irradiation time. Key as in Fig. 1 and the semiclosed points refer to samples with a HALS concentration 0·05%.

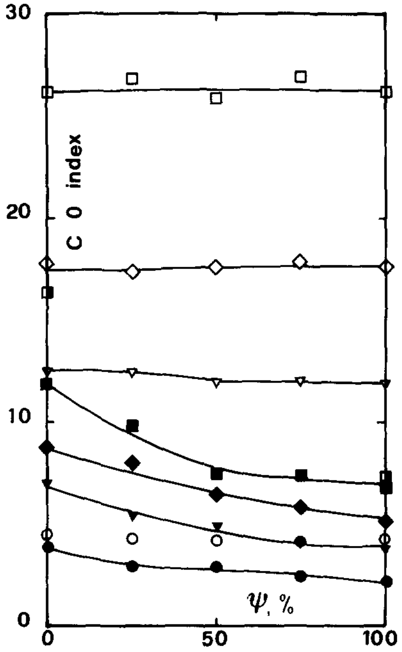

Fig. 3. Carbonyl index versus linear low density polyethylene content at fixed irradiation time. Key to symbols as in Fig. 2.

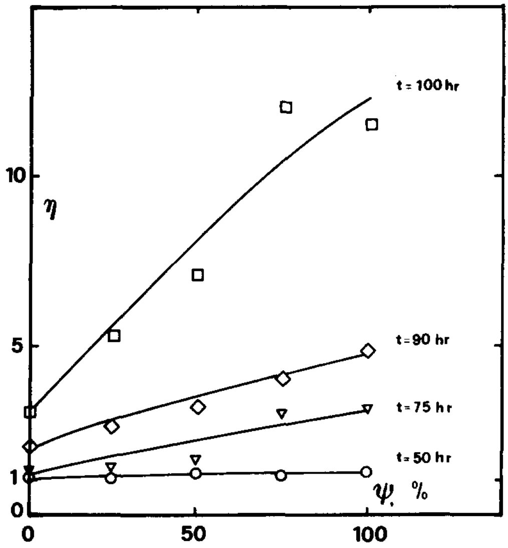

Fig. 4. η (see text) versus linear low density polyethylene content at fixed irradiation time.

stabilized films, the carbonyl index is smaller than that of the unstabilized samples and strongly dependent on the composition and, like the elongation at break, decreases with the LLDPE content.

The independence of the number of C═O groups from the composition is due to the fact that the two polymers have the same photo-oxidation kinetics because they have the same chemical structures, while the higher rate of degradation of the mechanical properties has been attributed[3] to the formation of long chain branching during the photo-oxidation in the linear polyethylene. The structure of LLDPE and its mechanical properties thus become very similar to those of the low density polyethylene.

As far as the stabilized films are concerned, the hindered amine, acting on the hydroperoxides or on the first steps of the photo-oxidation process, prevents the formation of long chain branching so that the elongation at break of LLDPE and of its rich blends also remains at high irradiation times.

The effectiveness of this stabilizer is well demonstrated by Fig. 4 where the dimensionless value:

$$\eta = \frac{\varepsilon(t, \mathrm{HALS})}{\varepsilon(t)}$$

has been plotted against the exposure time. η is defined as the ratio between the value of the elongation at break of the stabilized sample at a given irradiation time and the value of ε of the same unstabilized sample. Of course, the efficiency of the stabilization improves as the values of η increase.

TABLE 2
Compatibility of Spinuvex A36 in LDPE and LLDPE (Film thickness 100 μm)

Spinuvex (%)	*Time (days) to visible blooming at room temperature*	
	LDPE	*LLDPE*
0·25	207	>800

It is very obvious that the effectiveness of this hindered amine increases with the content of LLDPE and with the irradiation time.

All the above results show that this hindered amine works very well with the linear low density polyethylene and its effectiveness decreases with the content of low density polyethylene. This behaviour may be attributed to the presence of some catalyst residues (Ti $\simeq$ 12 ppm) acting as photo-oxidation promoters or to the better compatibility (see Table 2) of this UV stabilizer in the LLDPE sample which is then well dispersed in the matrix and especially in larger amount in the bulk of the polymer.

Confirmation of this latter hypothesis is given by two photo-oxidation tests carried out with the two homopolymers stabilized with one half of the concentration of this stabilizer. The elongation at break and the carbonyl index values are reported in Figs 2 and 3 as a function of the exposure time. The reduced amount of the stabilizer hardly changes the elongation at break or the carbonyl index of the LLDPE sample from that stabilized with 0·1% of the hindered amine.

On the contrary, the lower concentration of stabilizer has an important effect on the LDPE sample. There is a decrease in ε and a noticeable rise in the carbonyl index value with respect to the LDPE sample stabilized with the larger amount of amine. This probably means that part of the stabilizer is not available in the LDPE matrix due to the poor compatibility with this polymer.

CONCLUSION

The use outdoors of blends of low density polyethylene and linear low density polyethylene can be greatly improved by using sterically hindered amines as UV stabilizer.

A large improvement in the mechanical properties is obtained with a low concentration of this stabilizer. The effectiveness of the stabilizer increases with the content of linear low density polyethylene. This is probably due to the better compatibility of the hindered amine with the linear low density polyethylene matrix.

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