PHOTO-OXIDATION OF BLENDS OF POLYPROPYLENE WITH RECYCLED POLYPROPYLENE

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: الخلاصــة

تم دراسة تأثير عملية التأكد الضوئي على عدة مخاليط مصنعة من (البولي بروبلين) غير المؤكسد و (بولي بروبلين) المؤكسد ضوئياً من أجل التعرف على مدى تحمل هذه المواد لعوامل التعرية ومقارنتها مع مادة البولي بروبلين المصنع من البوليمري المعاد تصنيعه .
لقد لوحظ زيادة ظهور مجموعة (الهيدروكسيل) و (الكاربونيل) بزيادة تأثير عملية التأكسد بالضوء على (البوليمر) في المخلوط . كذلك أمكن وضع منحنى يبين علاقة تكوين مجموعة الكاربونيل بأزاحة بسيطة لمنحنى عدة مخاليط .

ABSTRACT

The photo-oxidation behavior of blends made with virgin polypropylene and photo-oxidized polypropylene has been studied in order to evaluate the weathering resistance of polymeric products made with recycled polymeric materials.

The formation of carbonyl and hydroxyl groups is strongly enhanced by the presence of photo-oxidized polymer in the blend.

A single master curve for the carbonyl formation rate can be constructed by a simple shift of the curves of the several blends.

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INTRODUCTION

The recycling of plastics waste is becoming more and more important because of the tremendous amount of plastic products which may possibly cause environmental pollution [1]. Unfortunately, not all polymeric materials can easily be recycled, for two main reasons. First of all, most of the polymers are incompatible without modifications of their surfaces, so the blends so obtained show very poor mechanical and physical properties. In the second place many polymers undergo several types of degradation, mainly mechanical and thermal degradation during processing and photo-oxidative degradation induced by the environmental agents and anomalous structures and impurities during their lifetime [2–5].

As for the blends obtained with recycled photo-oxidized material, their properties strongly depend on the amount and degree of photo-degraded components. In a previous work [6], the mechanical properties of blends of virgin polypropylene and photo-oxidized polypropylene have been studied and their behavior correlated with the resulting morphology. The presence of crystallites of different sizes gives rise to polymeric materials with poor mechanical properties (in particular the elongational at break) when the content of photo-oxidized material is more than 20%.

However, if these kinds of blends are to be used outdoors, the resistance to ultraviolet radiation must be taken into consideration.

In this work the photo-oxidation kinetics of blends of virgin polypropylene (PP) with photo-oxidized polypropylene (PPPh) has been studied as a function of the composition.

EXPERIMENTAL

The material used in this work was a polypropylene, commercially known as T30S manufactured and kindly supplied by Himont (Italy). The main properties of the raw material [7] are reported in Table 1.

This material was photo-oxidized in a Q.U.V. Accelerated Weathering Tester, manufactured by Q-panel Company (U.S.A.). The photo-oxidation was carried out using 8 UVB fluorescent lamps for 48 h. The cycle adopted was 8 h of ultraviolet irradiation at $T = 60°C$ and 4 h without irradiation at $T = 50°C$.

All the blends were prepared by melt-mixing the polymer parents in a Brabender Plasticorder model PLE 330 at $T = 180°C$ and 25 r.p.m. for about 20 min. The virgin polymer was also subjected to the same procedure.

The resulting material shows a lower molecular weight and a marked presence of oxygenated groups, in particular $C = O$ and $-OH$. Some properties of the photo-oxidized polypropylene are reported in Table 2 in comparison with those of the virgin material.

The investigated compositions, ψ, were 0, 25, 50, 60, 75, 90, 95, and 100 weight percent in virgin polypropylene.

Photo-oxidation of the blends was carried out using a xenon lamp (Osram XBO 150 W). The films were placed about 30 cm from the ultraviolet source. The dose rate was about $120 \, W \, m^{-2}$ as measured by means of an Eppley thermopile model G3.

Infrared absorption spectra were obtained by means of a Perkin–Elmer infrared spectrometer model 1420 linked to a Data Station Perkin–Elmer model 3600.

Table 1. Physico-Chemical Characteristics of the Raw Material

Sample Code	$[\eta]$ (dl/g)[a]	MFI (gr/10 min)[b]	$\overline{M}_w \, 10^{-3}$[c]	β[d]
PP2	2.00	3.0	390	8.6

(a) Intrinsic viscosity measured in tetrahydronaphthalene at 135°C.

(b) Melt flow rate, according to ASTM D 1238-73 method, procedure B.

(c) Weight average molecular weight, by Light scattering in α-chloronaphthalene at 150°C.

(d) Polydispersity ratio, by GPC in orthodichlorobenzene at 135°C.

Table 2. Physico-Chemical Properties of the Virgin PP2 Sample and of the Photo-Oxidized PP2 Sample

Sample Code	$\overline{M}_w \, 10^{-3}$	$C = O$ (mole l^{-1})
PP2	390	0.003
PPPh	80	0.02

The hydroxyl index was evaluated as the ratio of the absorbances at 3400 and 2730 cm^{-1}, in order to avoid the influence of variations of film thickness [8]. The carbonyl index was also evaluated as the ratio between the absorbances at 1710 and 2730 cm^{-1}.

RESULTS AND DISCUSSION

It is well known that the presence of oxygenated groups in macromolecular chains gives rise to rapid photo-oxidation of all polymeric materials and in particular of the polyolefines. The blends obtained by mixing virgin and photo-oxidized polypropylene show, of course, an initial number of hydroxyl and carbonyl groups depending on the blend composition.

Carbonyl and hydroxyl indices, indicative of C=O and −OH groups respectively, are reported in Figure 1. Within the experimental scattering, both values are almost linear with the composition.

The same values for all the samples are plotted as a function of the irradiation time in Figures 2 and 3 respectively.
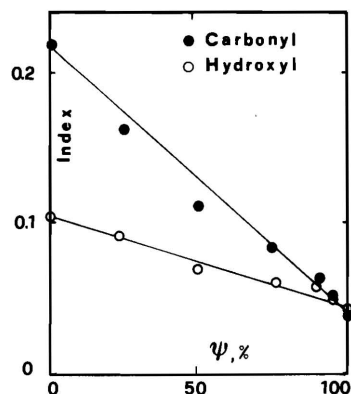

Figure 1. Carbonyl and Hydroxyl Index as a Function of the Virgin PP Content.

Both values rise rapidly on decreasing the amount of virgin polypropylene, showing once again that the presence of C=O and −OH groups in the blends lowers noticeably the photo-oxidative resistance of the polymeric materials. As for the pure material after 24 h of exposure, the formation of both oxygenated groups does not reach the initial value of the blends with more than 50% of photo-oxidized component. In particular the concentration of carbonyl groups after 24 h of photo-oxidation in the
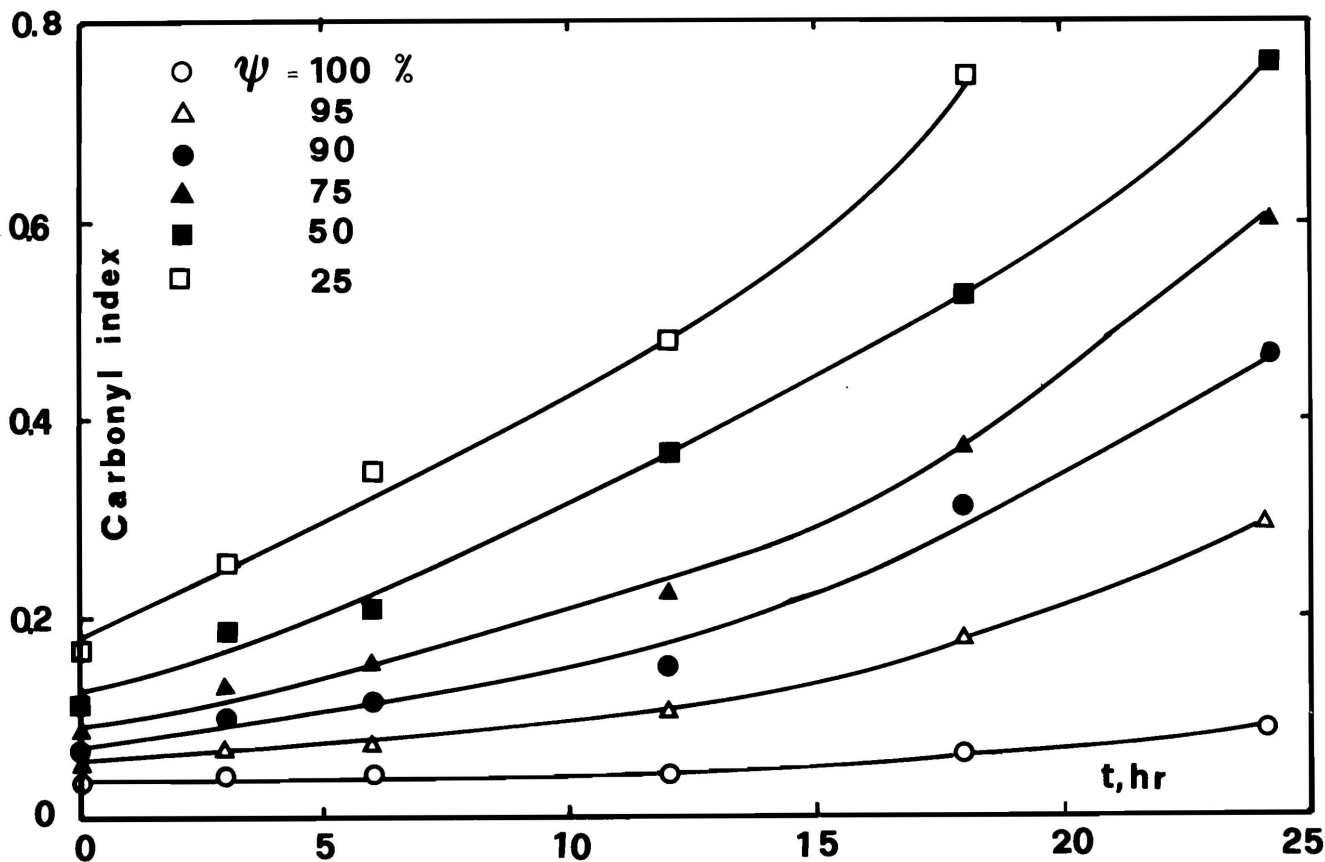

Figure 2. Carbonyl Index as a Function of the Irradiation Time.

virgin material is lower than the initial value of the blend with only 25% of degraded polymer.

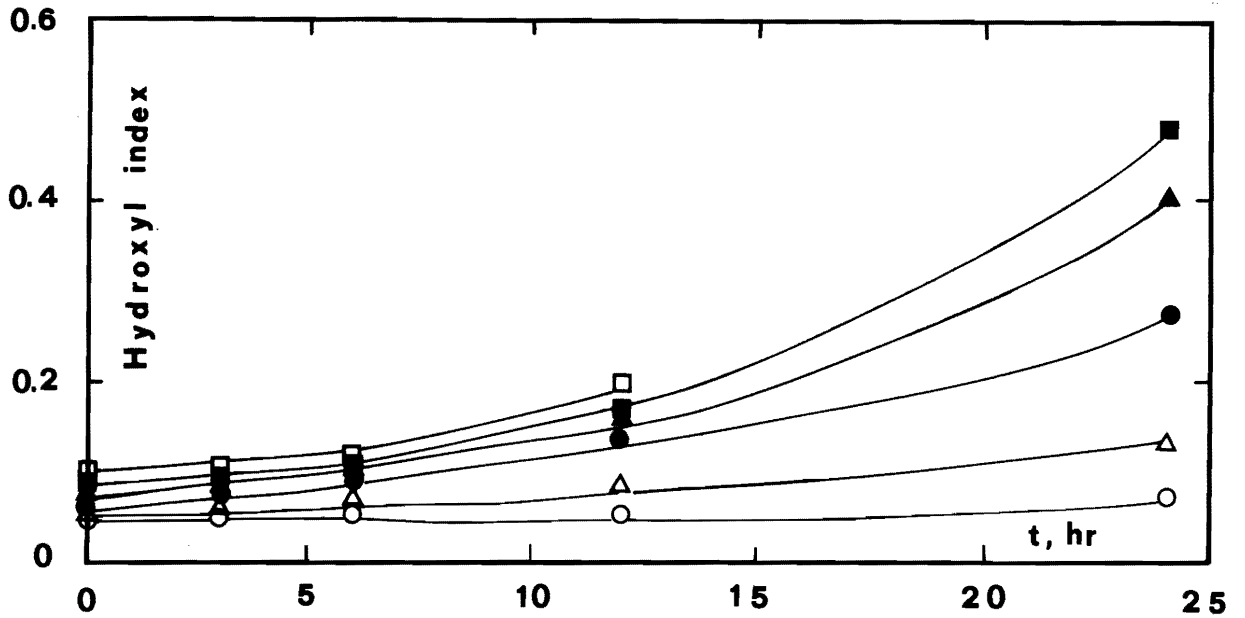In Figure 4 the dimensionless values of the carbonyl index

Figure 3. Hydroxyl Index as a Function of the Irradiation Time. Key to Symbols as in Figure 2.
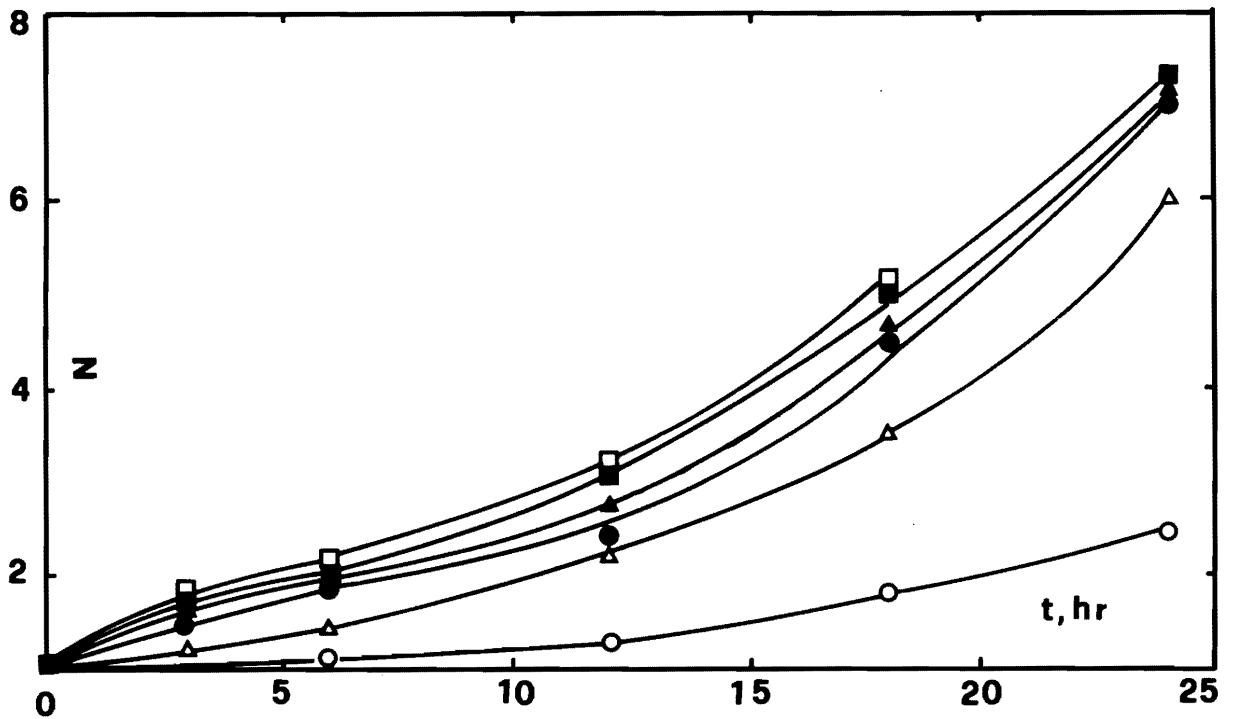

Figure 4. Dimensionless Carbonyl Index as a Function of the Irradiation Time. Key to Symbols as in Figure 2.

$$N = \frac{\text{Carbonyl index } (t)}{\text{Carbonyl index } (t=0)} \qquad (1)$$

of all the samples are plotted against the irradiation time.

At the beginning of the process, the different samples show very different photo-oxidation kinetics and more and more faster on increasing the amount of PPPh.

On the contrary, the blends containing less than 10% virgin polypropylene reach about the same dimensionless values at the end of the irradiation time. This means that, at a given time, when the samples contain a large number of C=O groups, very higher than the initial one, the photo-oxidation kinetics is very similar for all the samples.

The initial slope of these curves can be considered as the kinetic constant of the photo-oxidative reaction and K values were estimated. In Figure 5 these constants are plotted as a function of the composition. The value of K decreases almost linearly with the content of virgin PP up to about 90%, while it falls suddenly at a content higher than 90%.
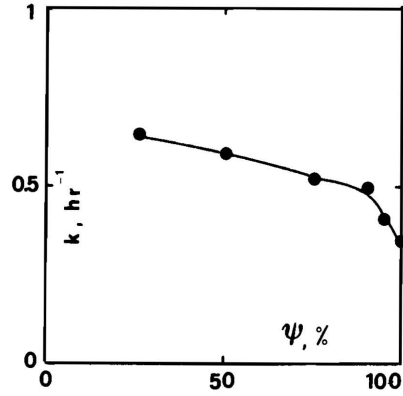

Figure 5. Kinetic Constant as a Function of the Virgin PP Content.

Looking again at Figure 2, the transient curves of the formation of the carbonyl groups show about the same form, and a shift along the time axis, with respect to the curve of the virgin PP, gives rise to a single master curve, which is shown in Figure 6. The good superposition of the curves is clearly evident from the graph. The shift time, t_s, determined from the shift along the time axis necessary to obtain a good superposition, indicates that the presence of C=O groups acts as a "catalyst" decreasing some-
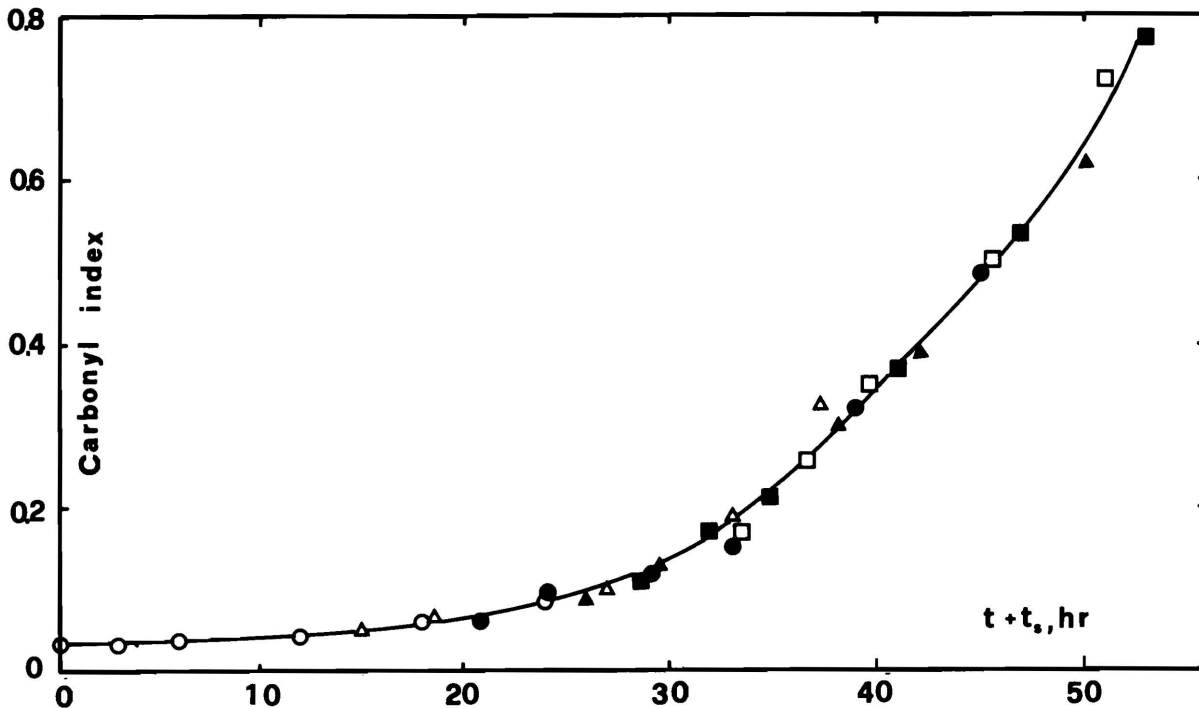

Figure 6. Master Curve of Carbonyl Index as a Function of the Time. Key to Symbols as in Figure 2.

times to zero, the induction time for the photo-oxidation reaction. In other words, on increasing the number of C=O groups, their formation rate becomes the same as that for a sample with less initial carbonyl groups but at a higher irradiation time.

The shift time depends on the composition as plotted in Figure 7. As for the kinetic constant, in this case also, t_s changes slowly when $\psi \leqslant 90\%$ and then falls rapidly.
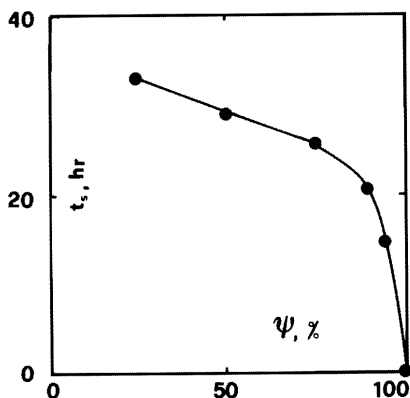

Figure 7. Time Shift as a Function of the Virgin PP Content.

CONCLUSION

The reuse of photo-oxidized polymers by blending with virgin material gives rise to a polymeric material whose weathering resistance is more and more poor as the content of recycled material increases.

The carbonyl formation rate can be described by a single master curve obtained by shifting the original curves of the different blends. This time shift depends on the C=O content and on the composition of the blend.

ACKNOWLEDGEMENT

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