

Blends of Nylon 6 with a Polyethylene Functionalized by Photooxidation

D. CURTO, A. VALENZA, and F. P. LA MANTIA, *Dipartimento di Ingegneria Chimica dei Processi e dei Materiali, Università di Palermo, Viale delle Scienze, 90128 Palermo, Italy*

Synopsis

An easy and cheap method to prepare functionalized polyethylene is reported in which polyethylene is photooxidized and then melt-blended with nylon. Structural, rheological, and mechanical modifications indicate that carbonyl, formed during photooxidation, and amine groups react giving rise to copolymers which stabilize the blends. Photooxidized polyethylene from waste could be very effective in preparing polyethylene/polyamide blends with improved properties. This new approach improves over current methods in which compatibilization of polyolefines and polyamides is mostly performed by reacting functionalized polyolefines with polyamides in molten state. The functionalization is achieved by chemical modification of the polyolefines chains. This step could be very expensive.

INTRODUCTION

Polymer blends are a class of polymeric systems which can achieve two important purposes, namely, to obtain materials with a good range of properties with a low cost/price ratio and to allow the recycling of degraded polymeric materials.¹⁻⁵ Unfortunately, most polymers, having chemical structures strongly different, are incompatible and their resulting properties are very modest and frequently worse than those of the parent polymers.

Among these polymeric systems, the blends of polyamides and polyolefines are particularly interesting. Indeed, the polyolefines improve the impact resistance, especially at low temperatures, of the polyamidic matrix, and, on the other hand, the polyamide can improve the resistance to oxygen permeation which prevents the use of polyolefines as barrier films.

Many efforts have been devoted to compatibilize the blends of polyolefines and polyamides,⁶⁻¹⁰ which, because of their strong incompatibility, give rise to products with very low mechanical properties. Most of these methods consider functionalized polyolefines which can react with the amine groups of polyamides, giving rise to copolymers stabilizing the blends. This functionalization is mostly performed by chemical modification of the polyolefines structure. This step is, in general, long and expensive.

In this work a new method of functionalizing the polyethylene is proposed. The polyethylene is previously photooxidized and then blended with nylon 6. Structural, rheological, and mechanical determinations indicate that carbonyl and amine groups react, giving rise to copolymers which stabilize the blends.

EXPERIMENTAL

The materials used in this work were a low density polyethylene (LDPE) and a polycaprolactam (Ny 6) manufactured by ENICHEM and SNIA (Italy), respectively. The main physicochemical characteristics of the raw materials are reported in Table I.

The low density polyethylene has been photooxidized in a Q.U.V. Accelerated Weathering Tester, manufactured by Q. Panel Company (U.S.A.).

The photooxidation was carried out using eight U.V.B. fluorescent lamps for 24, 48, and 72 h. The cycle adopted was: 8 h of ultraviolet irradiation at $T = 60^\circ\text{C}$ and 4 h of condensation at $T = 50^\circ\text{C}$. This cycle was used both in order to increase the photochemical effects and to permit condensation exposure to reach equilibrium.

All the blends were prepared by melt mixing the homopolymers in a Brabender Plasticorder Model PLE 330 at $T = 240^\circ\text{C}$ and at 150 rpm. The mixing time was about 15 min, enough to get a practical constant value of the torque. Also the homopolymers were subjected to the same treatment.

The polyamide content of the blends was 75% wt/wt. Four blends were prepared using LDPE both virgin and photooxidized for different time period: PEPH0 (not photooxidized), PEPH24, PEPH48, and PEPH72, photooxidized 24, 48, and 72 h respectively.

Structural Determinations

Photooxidized low density polyethylene samples were characterized considering the carbonyl groups and the gel fraction formed during irradiation.

Carbonyl groups were determined using infrared spectroscopy by means of a Perkin-Elmer IR spectrometer Model 1426 linked to a Data Station Model 3600. The carbonyl concentration was evaluated considering the peak at 1718 cm^{-1} and an extinction coefficient of $300\text{ L mol}^{-1}\text{ cm}^{-1}$.

The gel content was determined by means of a Soxhlet extractor. Approximately 0.3 g of any photooxidized polyethylene sample was exposed to refluxing p-xylene close to its boiling point for 48 h.

TABLE I
Physicochemical Properties of the Raw Materials

	LDPE	NY 6
MFI (g/10 min) ^a	0.08	10.8
$M_w \times 10^{-3}$	450	37
$\beta = M_w/M_n$	7.2	2.1
$[\eta]$ (dL/g) ^b	0.95	—
η_{rel} ^c	—	2.60
ρ (g/cm ³)	0.919	1.141
$[\text{NH}_2]$ (meq/kg)	—	55

^aASTM D 1238/73 method, procedure B and procedure Q.

^bIn tetrahydronaphthalene at 130°C .

^cIn formic acid at $T = 30^\circ\text{C}$.

^dASTM D 1505/78 method.

The samples, fractured under liquid nitrogen, were observed with a scanning electron microscope, Philips Model 505. The surface of the specimens were coated with gold.

Molau tests⁹ were carried out by dissolving 200 mg of sample in 10 mL of 80% formic acid.

Rheological and Mechanical Determinations

The melt flow index of all the samples was determined using a melt indexer CEAST (Italy) under a force of 2.16 kg. For all the blends and for the homopolymer samples the test temperature was 230°C.

Tensile properties measurements were carried out by means of an Instron machine Model 1122 at room temperature. A crosshead speed of 5 cm/min and a gauge length of 3 cm were used in all measurements.

The specimens used for tensile tests were cut out from sheets obtained by compression molding at $T = 240^{\circ}\text{C}$ (180°C for the pure polyethylene). Before testing, the specimens were equilibrated in ambient conditions ($T = 20^{\circ}\text{C}$ and 60% R.H.) for at least 3 days.

All the reported results are an average of at least 10 measurements.

RESULTS AND DISCUSSION

In Table II some physical properties of all the polyethylene samples are reported. As is well known, low density polyethylene undergoes, during photooxidation, many dramatic modifications of both structure and morphology. In particular, increase of carbonyl groups, change of molecular weight, and formation of crosslinking are well established.¹¹ The photooxidized samples used in this work show all these features and both gel fraction and C=O groups increase with photooxidation time.

Figure 1 shows the results for the Molau tests. The solution is clear for the blend PEPH0/Ny. This solution consists of nylon 6 soluble in formic acid. The upper part of the same test tube is a suspension of polyethylene particles. The tests relative to the blends containing photooxidized polyethylenes show, on the contrary, an increasing and persistent turbidity, which represents a suspension of colloidal particles.

Following Molau and other authors,^{9,10,12} this colloidal suspension should be due to the existence of LDPE/Ny6 graft copolymers acting as interfacial agents. In our cases we believe that, during melt blending, chemical reactions between carbonyl groups (formed during photooxidation of polyethylene) and amino groups of nylon 6 occurred.

TABLE II
Physicochemical Properties of the Polyethylene Samples

Sample code	MFI (g/10 min)	gel %	C=O (mol L ⁻¹)
PEPh 0	0.08	0	0
PEPh 24	—	11	0.07
PEPh 48	—	19	0.11
PEPh 72	—	25	0.28

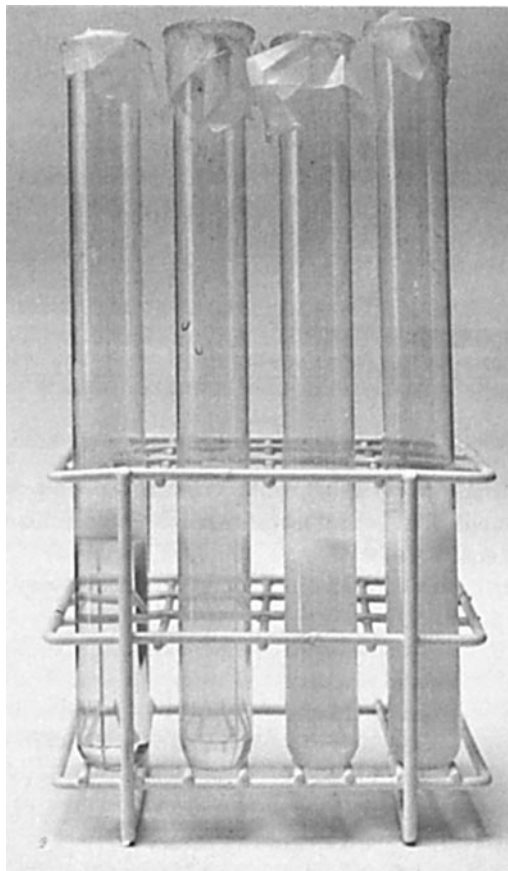


Fig. 1. Molau tests. From left to right: PEPH0/Ny, PEPH24/Ny, PEPH48/Ny, and PEPH72/Ny.

Considering that a remarkable part of these carbonyl groups are —COOH groups,¹³ the most probable reaction occurs between carboxyl and amino end groups. In order to have such reactions the end amine groups should be, then, available for reacting with carboxyl groups. However, some reactions with the amidic groups cannot be excluded at this temperature.

The suspension turbidity increases as the photooxidation time of the polyethylene rises and then, of course, with the growth of carbonyl groups, as reported in Table II, agents between chains of soluble (Ny 6) and insoluble (LDPE) homopolymers. Its stability and degree of turbidity is a measure of the amount of copolymer in the mixture.

The SEM microphotographs of the cryogenically fractured surfaces of tensile specimens are given in Figures 2–5 for the blends with the four samples of both virgin and photooxidized polyethylenes.

In the blend containing PEPH0, the polyamide is the continuous phase and the polyethylene forms the discrete phase. The polyethylene particles have average dimensions ranging from 5 to 10 μm . The microphotographs of the blends containing photooxidized polyethylenes show an almost homogeneous phase and are hardly distinguishable as the result of good dispersibility.



Fig. 2. SEM microphotograph of the sample PEPH0/Ny

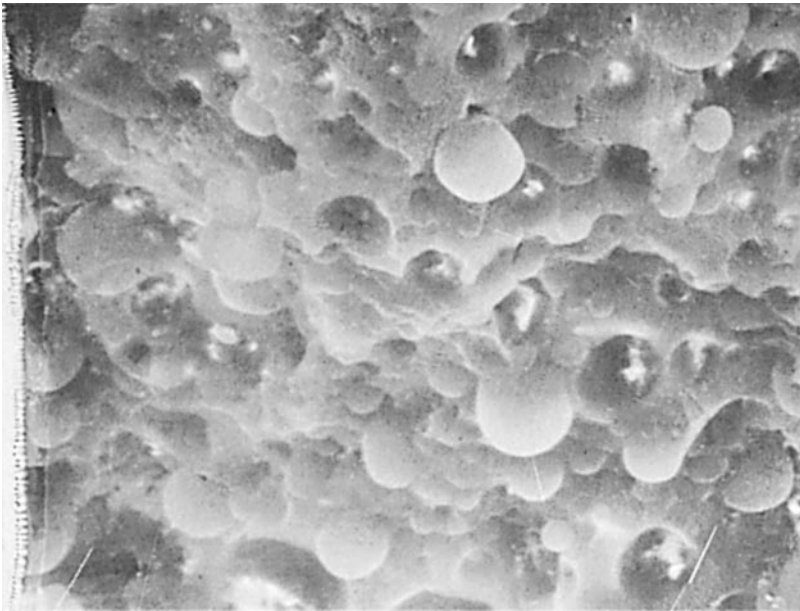


Fig. 3. SEM microphotograph of the sample PEPH24/Ny



Fig. 4. SEM microphotograph of the sample PEPH48/Ny

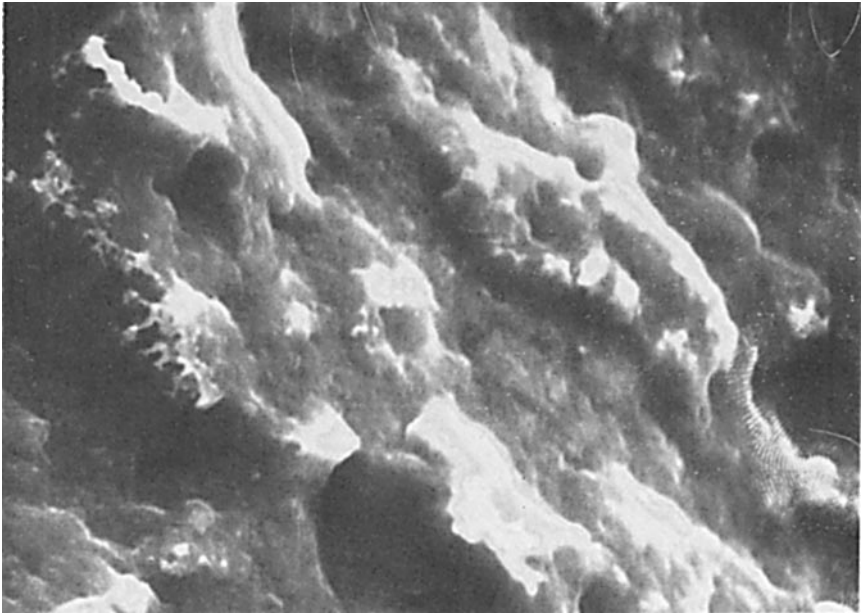


Fig. 5. SEM microphotograph of the sample PEPH72/Ny

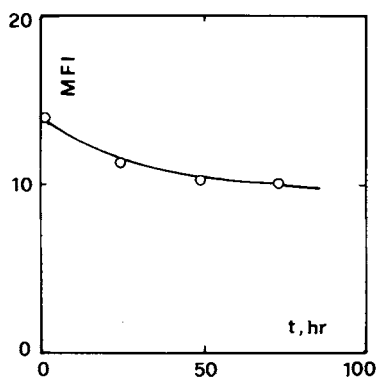


Fig. 6. Melt flow index of blend vs. photooxidation time of the polyethylene.

The SEM microphotographs are consistent with the proposed chemical reactions between carboxyl groups and amino end groups forming a graft copolymer. This copolymer acts as interfacial agent between continuous and dispersed phases. The presence of such an interfacial agent causes smaller dimensions of the dispersed particles and a good adhesion between discrete and continuous phases.

The plot of the melt flow index versus the photooxidation time of the polyethylene is shown in Figure 6. The melt index of the blend with the unirradiated polyethylene is intermediate with respect to the neat polymers and decreases as the photooxidation time increases. In the first case the lack of compatibility between the two phases gives rise to a blend with lower viscosity; the decrease of the melt index (rise of the viscosity) indicates a small deformability of the macromolecules. This is due again to the good adhesion between matrix and discrete phase, and, because the number of C=O groups increases with photooxidation time, one should expect more chemical reactions in the blend with the more photooxidized polyethylene and thus stronger interfacial adhesion.

Elastic modulus E , tensile strength σ_{b_0} , and elongation at break, ϵ_b , are reported in Figures 7-9 as a function of the irradiation time of the minor component. The elastic modulus of the blends increases as the photooxidation time of the polyethylene rises. This improvement is attributed to the chemical

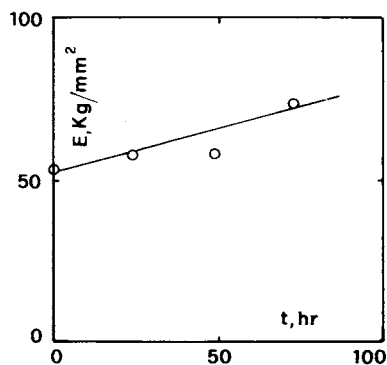


Fig. 7. Elastic modulus of blend vs. photooxidation time of the polyethylene.

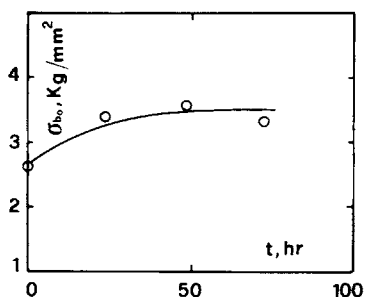


Fig. 8. Tensile strength of blend vs. photooxidation time of the polyethylene.

reactions occurring during melt blending which form, as mentioned above, a reinforcing interphase between the two polymers.

Similar comments can be made for the tensile strength, which, however, seems to reach a plateau at high photooxidation times.

The elongation at break shows a more complicate trend. There is a rapid increase of ϵ_b as the photooxidation time of the polyethylene increases, but also a decrease after 50 h of photooxidation is observed. It should be noted that the elongation at break of the polyethylene, reported in the same figure, decreases with increasing the amount of photooxidation because of both the superficial defects grown during the irradiation¹⁴ and the presence of increasing amount of crosslinked macromolecules. Then the ϵ_b value of the blend PEPH72/Ny decreases due to the low elongation at break of the more photooxidized polyethylene.

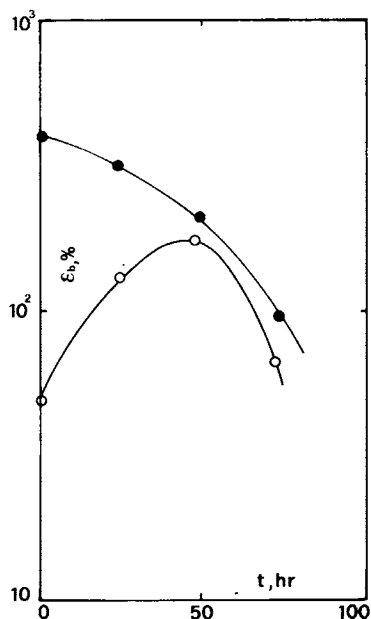


Fig. 9. Elongation at break of the pure LDPE (●) and of the blend (○) vs. photooxidation time of the polyethylene.

The initial increase of the elongation at break confirms again the presence of an interphase between the two phases induced by chemical reactions during melt blending.

CONCLUSIONS

The low compatibility between polyethylene and polyamide can be improved by photooxidizing the polyethylene. The C=O groups, in particular the carboxylic groups, react with the amino end groups during melt blending, giving rise to graft copolymers which act as interfacial agents. Both physicochemical tests and mechanical measurements confirm this hypothesis. The blends of polyamide and photooxidized polyethylene show larger viscosity and better mechanical properties than those made with virgin polyethylene.

All the above results suggest the possibility of using photooxidized polyethylene, originating in particular from waste, as a functionalized polymer for preparing polyethylene/nylon blends with improved physical properties.

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