



Effect of compatibilization on the photo-oxidation behaviour of polyethylene/polyamide 6 blends and their nanocomposites



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ABSTRACT

Polymer based nanocomposites are increasingly attracting interest from academia and industry, and the use of polymer blends as matrices greatly increase their potential field of application. In order to improve their characteristics, the use of compatibilizers acting on the blend components is mandatory. However, this also leads to rising concerns regarding the behaviour of polymer blend based nanocomposites upon being subjected to photo-oxidative degradation. It is known that morphology can deeply influence the photo-oxidative behaviour, and this can be therefore deeply influenced by the blend components and by the use of compatibilizers.

In this work, polymer blend nanocomposites, based on low density polyethylene and polyamide 6 have been prepared, containing organically modified clay as nanosized filler and two different functionalized polymers as compatibilizers, and processed in a film blowing operation in order to evaluate the effect of the compatibilization on photo-oxidation.

The presence of the compatibilizer significantly improves the photo-resistance of the blend, while this improvement is less relevant in the nanocomposites since the photo-oxidation rate seems to be mainly dependent on the clay content and its direct effects on the photo-oxidative phenomena.

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1. Introduction

Polymer based nanocomposites have been attracting an increasing interest over the last years, both from the academia and the industry [1–3], thanks to several enhancements in technological properties (such as elastic modulus, barrier properties, etc.) which can be achieved even with small amounts of nanometric sized fillers [2,4–6]. A further improvement can be obtained by using polymer blends as matrix, in replacement for single polymer matrices. These can provide new matrices with tailored characteristics and can be obtained by common processing techniques; on the other hand, the most important limitation is related to the possible incompatibility between the two (or more) components of the blends, since the majority of the polymers typically used for technological applications are thermodynamically immiscible and incompatible, leading to a dramatic worsening of the properties [7–10]; this leads to the use of compatibilizers.

However, the above mentioned, increasing interest towards polymer nanocomposites in the industrial field is currently leading to new concerns regarding the degradation behaviour of these systems, including both thermomechanical [10] and photo-oxidative degradation.

The photo-oxidation behaviour of polymer blends is a very challenging topic, since it depends not only on the photo-oxidation kinetics of the two components, but also on the reactions between the degradation products of the two components, as well as the reactions between the degradation products of each polymer with the macromolecules of the other components [10–16]. In the same way, the photo-oxidation of polymer nanocomposites depends also on the interactions between polymer matrix and nanoparticles. In particular, the organo-modified clays can strongly change the photo-oxidation kinetics of the polymer matrix because of the presence of iron ions in the clay [17], although it has also been found that clays deprived of iron ions can influence the photo-oxidation behaviour as well, due to absorption of additives and antioxidants [18], a mechanism that can obviously occur also when iron-containing clays are used [19].

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In general, the degradation of clay-filled nanocomposites is strongly affected by the presence of these fillers [20–23]; this does not regard only the photo-oxidation behaviour, but also the thermomechanical degradation, which is clay dependent because of the degradation of the organo-modifier at relatively high temperatures [10,24].

Both blends and nanocomposites are often compatibilized with a third component in order to improve the adhesion between the different phases [7–9,25–35] and, in this case, the presence of this component can change the photo-oxidative degradation path of the uncompatibilized material [14,20–23,36,37].

The effect of the change of morphology due to the change of crystallinity, orientation and compatibilization of blends and of polymer blend nanocomposites (dispersion, dimensions and adhesion) on the degradation behaviour of polymer systems has not received much attention in the Literature [38–40]. These studies have shown that the influence of the above mentioned factors on the degradation behaviour of polymer blends and nanocomposites is quite complex involving, for instance, the thermal decomposition products of filler modifiers, the possible photo-instability of compatibilizers, unfavourable interactions between the compatibilizer and polymer/filler degradation products, different interactions between the polymer matrix components and the filler due to the modified dispersion of the latter.

Aim of this work is, therefore, to evaluate the effect of the compatibilization on the photo-oxidation behaviour of PA/PE blends and of their nanocomposites containing an organo-modified clay. In particular, the influence of the compatibilizer on the photo-resistance of the blend was directly compared to that in the nanocomposites.

2. Experimental

The PA6 used for this work was a sample of Radilon S35 100 NAT, kindly supplied by Radicinova (Italy) with an intrinsic viscosity (measured in sulfuric acid) equal to 3.4 dl/g. The LDPE was a film blowing grade (FC39, Versalis, Italy) having an MFI of 0.36 g/10 min. The two functionalized polymers used as compatibilizing systems were: a maleic anhydride grafted SEBS (styrene-ethylene-butylene-styrene) copolymer (Kraton 1901X) and a glycidymethacrylate-ethylene copolymer (Lotader AX8840). A 5 wt% of a clay modified with alkylammonium salts (Cloisite 15A, Southern Clay) was added to the blend. The organic modifier is a dimethyl-ditallow, with two organophilic tails fully hydrogenated with an average composition of 65% C₁₈, 30% C₁₆ and 5% C₁₄. In order to prevent the hydrolytic chain scission, PA6 was dried for 10 h in a ventilated oven at 90 °C followed by 16 h under vacuum at 120 °C.

Blends of PA6/LDPE 25/75 w/w were produced by using a corotating modular twin screw extruder (OMC, Italy). The materials were prepared by premixing them in the solid state and then feeding them into the extruder. The thermal profile chosen for processing was 180–200–210–220–230–240–240 °C and the screw speed was 220 rpm. Films of the blend and of the nanocomposite samples were obtained by film blowing process carried out with a Brabender (Germany) single screw extruder ($D = 19$ mm, $L/D = 25$) at a thermal profiles of 180/200/220/240 °C and the screw speed was set at 60 rpm. The extruder was equipped with a film blowing head and a Brabender film blowing unit. The blow up ratio, BUR, was about 4 for all the blown samples and the draw ratio, DR, about 5.

The films were photo-oxidized in a Q.U.V. Accelerated Weathering Tester, manufactured by Q-panel Company (U.S.A.). Photo-oxidation was carried out using 8 UVB fluorescent lamps up to

approximately 200 h. The adopted cycle consists of 8 h of ultraviolet irradiation at $T = 55$ °C and 4 h without irradiation at $T = 40$ °C.

The morphology of the nanocomposites was evaluated by using scanning electron microscopy (SEM) on samples fractured in liquid nitrogen and covered with gold to make them conductive, using an FEI (U.S.A.) Quanta 200F scanning electron microscope.

FTIR analysis was carried out using a Spectrum One (PerkinElmer, UK) equipment in order to record FTIR spectra of the specimens, using 16 scans at a resolution of 1 cm⁻¹ (in the range 450–4000 cm⁻¹). Measurements were obtained from the average of triplicate samples, with a calculated maximum experimental error (relative standard deviation) of approx. 5%.

Mechanical characterization was carried out on specimens cut off from compression-moulded sheets ($10 \times 90 \times \sim 0.6$ mm) and from films in the machine direction and tested using an Instron (USA) 3365 tensile testing machine according to ASTM D882. The grip distance was 50 mm and the crosshead speed was 50 mm/min. The reproducibility was satisfactory ($\pm 8\%$).

Differential scanning calorimetry (DSC) measurements were performed by using a Shimadzu (Japan) DSC-60 apparatus, under nitrogen flow with a temperature range from 30 to 250 °C at 10 °C/min rate and a $\pm 6\%$ reproducibility.

Oxygen permeation tests were performed in gas–membrane–gas configuration apparatus based on the measurement of the pressure increase of the downstream side of the sample, while maintaining a

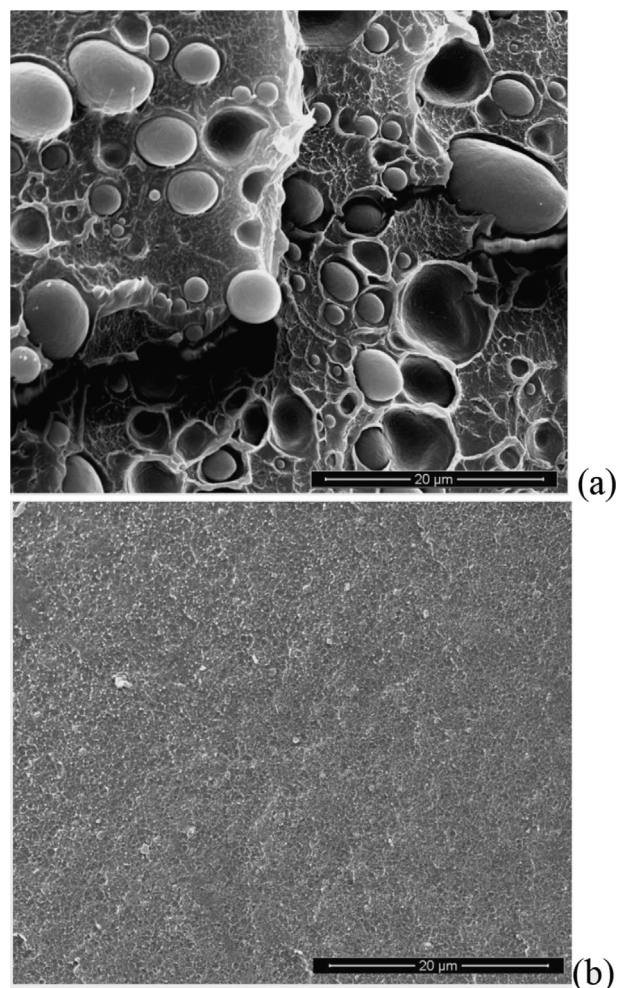


Fig. 1. SEM micrographs of the uncompatibilized (a) and compatibilized with Kraton (b) polymer blends.

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