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Influence of Natural Weathering on the Physical Properties of Compatibilized Blends of Poly(propylene)/Polyamide-6

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Summary: The present paper deals with the effects of natural weathering on the properties of poly(propylene)/polyamide-6 blends (70/30 wt %) without and with PP-*g*-MA used as the compatibilizer at various content ratios (2, 4 and 6 wt%). The resulted changes in the chemical structure, morphology and mechanical properties of the different blends were analyzed by Fourier transform infrared (FT-IR) spectroscopy, scanning electron microscopy (SEM), and tensile tests. After one year of outdoor exposure, no important changes in the chemical structure are observed by FT-IR spectroscopy for both virgin and compatibilized blends. SEM analysis revealed the effectiveness of PP-*g*-MA to improve the compatibility of PP/PA-6 blends. However, the weathering effect on the morphology of both virgin and compatibilized blends resulted in the formation of voids and cracks on the fracture surfaces, while the ultimate tensile properties decreased considerably. The overall results indicated clearly that the presence of PP-*g*-MA compatibilizer in PP/PA-6 blends had no influence on the photo-oxidation process.

Keywords: blends; degradation; mechanical properties; morphology

Introduction

Among immiscible polymer blends of technological interest, blends of poly(propylene) and polyamide-6 have received much attention because of their improved chemical and mechanical characteristics.[1] The pseudo-ductile polymer, PP, has good overall mechanical performances, good moisture resistance and low cost, but it shows relatively poor chemical and heat resistance.[2] On the other hand, PA-6 is an excellent engineering plastic with good abrasion resistance and electrical properties. However, it has a high cost and a considerable water sorption.[3] PA-6 is also known to be a notch-sensitive thermoplastic owing to a markedly lower resistance to crack propagation than to crack initiation.[2] Unfortunately, the two polymers are not miscible, so that a third component, i.e. a compatibilizer, has to be added in order to improve their interfacial adhesion and to enhance the material homogeneity.[4] Maleic anhydride grafted polypropylene (PP-*g*-MA) is the most widely used compatibilizer for PP/PA-6 blends due to its ability to form a chemical linkage through the reaction of anhydride groups with the polyamide end groups.[5] The commercial importance of such polymer blends implies interest in knowledge of their degradation behaviour under environmental conditions. Indeed, polymeric materials undergo irreversible structural changes in their lifetime as a result of their exposure to environmental factors, mainly UV light, oxygen and heat.[6] In this respect, the literature[3,6,7] reported that

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the photo-oxidation of polymer blends is a complex phenomenon, since both components are susceptible to oxidation. As a result, radical species can be formed in the two homopolymers and these species can interact. The extent of degradation depends also on the presence of additives in the blends such as stabilizers and compatibilizers. Furthermore, the diffusion of oxygen is another parameter to be taken into consideration in the characterization of the photo-oxidation mechanism due to the fact that it can differ from one of the blend components to the other. The mechanisms by which photo-oxidation occurs in both PP and PA-6 can be considered as fairly well understood.[8,9] However, in spite of the considerable work carried out on the degradation of neat polymers, there are only a few papers which deal with photo-oxidation of polymer blends and particularly those based on PP/PA-6. Therefore, the present work is aimed to investigate the natural weathering effects on the chemical structure, the morphology and the mechanical properties of blends based on PP/PA-6: 70/30 (wt%) compatibilized with PP-*g*-MA at various content ratios, i.e. 2, 4 and 6 wt%. The degradation of the samples under natural weathering was evaluated by several techniques involving FT-IR spectroscopy, SEM, and tensile tests.

Experimental Part

Materials

The PP used is an isotactic homopolymer produced by INEOS Olefins and Polymers Europe (United Kingdom) under the trade name 100-GA03. The polymer has the following characteristics as provided by the manufacturer: a melt flow index = 3 g/10 min (at 230 °C and 2.16 kg), a melting point = 163 °C and a Vicat softening point = 156 °C.

PA-6 was supplied by Lanxess (Germany) under the trade name Durethan B 30 S. PA-6 has a melting temperature of 222 °C, a density of 1.14 g/cm^3, a water absorption = 10%, a moisture absorption at equilibrium = 3% and a melt flow index = 102 g/10 min.

The compatibilizer used was PP-*g*-MA from DuPont International S.A. (Australia) under the trade name Fusabond^R P M613–05. The maleic anhydride content is less than 0.1 wt%. The main characteristics of the compatibilizer are a melt flow index of 120 g/10 min, a melting temperature of 162 °C and a decomposition temperature higher than 250 °C.

Preparation of Samples

Melt compounding of PP/PA-6 blends was performed on a Bauzano counter rotating twin screw extruder (Italy) with a ratio L/D = 19. The processing temperature was 240 °C, whereas the screw rotational speed was 40 rpm. Prior to extrusion, PA-6 pellets were dehumidified in a Moton MDE 40 Desiccant dryer at 90 °C for 3 hours. All the blend components, i.e. PP, PA-6 and PP-*g*-MA were premixed together before addition to the hopper of the extruder according to the compositions reported in Table 1. The extrudates were grinded and injection moulded into standard specimens (ISO 527-2) using a Bettenfeld Unilog 4000 (200 CD) injection molding machine (Germany). The temperature setting along the zones of the injection unit ranged from 220 to 240 °C. Prior to injection molding, PA-6 and all the blend materials were dried at 90 °C for 3 hours.

Natural Weathering

Natural weathering of PP/PA-6 blend samples was carried out according to ASTM D 1435. The specimens were mounted 45°, facing the south direction.

Table 1.
Code and composition of various PP/PA-6 blends.

Code	PP (wt %)	PA-6 (wt %)	PP-*g*-MA (wt %)
PP/PA-6/0C	70	30	0
PP/PA-6/2C	68	30	2
PP/PA-6/4C	66	30	4
PP/PA-6/6C	64	30	6

The exposure was carried out at M'sila, which is a high land city located on the south east of Algeria (latitude 35° 40′N and longitude 04° 30′E). The samples were exposed for 1 year from July 2008 to June 2009. The average radiation in the experimental period was 400 kcal/cm^2/year. The average temperature varied between 12 (winter) and 40 °C (summer). The humidity level varied between 88 (winter) and 37% (summer) and the amount of rain was 17 mm/year.

Characterization Methods

Infrared spectra were recorded using a Shimadzu Irraffinity-1 spectrometer with 4 cm^{-1} resolution and 40 scans. All spectra were recorded in the absorbance mode in the 4000-600 cm^{-1} region. The tensile tests were carried out using a Zwick/Roell Z 250 machine at 23 °C according to ISO 527-2, with a crosshead speed of 50 mm/min. Prior to testing, all specimens except PP ones were dried at 90 °C for 3 hours. Tensile strength and elongation at break were evaluated from the stress-strain data. The morphology of PP/PA-6 blends was observed with a Philips XL30 scanning electron microscope (SEM) operated at 15 kV. SEM micrographs were taken from fractured surfaces of samples after submersion in liquid nitrogen.

Results and Discussion

FT-IR Spectroscopy Analysis

The changes in the chemical structure of PP, PA6 and PP/PA-6 blends with and without PP-*g*-MA were examined by FT-IR spectroscopy after 1 year of outdoor exposure. FT-IR data indicated the formation of both C=C stretching vibration and carbonyl groups in the exposed samples of PP. According to Rivaton et al.,[8] the mechanism by which the photo-oxidation occurs in PP involves an induced oxidation of the tertiary carbon atoms that accounts for the formation of tertiary hydroperoxides which can further decompose to carbonyl products. For PA-6, it was noted in the exposed samples, the formation of imide groups.[7] Moreover, as suggested by Tang et al.,[12] the radical attack on the polyamide backbone occurs at the N-vicinal methylene groups –CONH–CH$_2$–, leadings to the formation of hydroperoxides. For PP/PA-6/0C blend without compatibilizer, the FT-IR data showed the presence of two characteristic bands at 1640 and 1540 cm^{-1} before exposure due to amide groups.[13] Furthermore, the FT-IR spectra of PP/PA-6 blends containing 2, 4 and 6 wt% of PP-*g*-MA exhibited almost similar shape with the uncompatibilized one suggesting that PP-*g*-MA had probably reacted with PA-6 resulting in the formation of grafted copolymer at the interface through the imide linkage.[14] After 1 year of outdoor exposure, no important changes in the chemical structure are observed by FT-IR spectroscopy for both uncompatibilized and compatibilized blends. This result means that the compatibilizer had no noticeable effect on the degradation process.

Tensile Measurements

The elongation at break is commonly used to investigate the photo-oxidation behaviour due to its sensitivity to the structural and morphological variations of the materials occurring during the aging process.[3] Figure 1 shows the variation of elongation at break of blend PP/PA-6 as a function of PP-*g*-MA content before and after 1 year of exposure. From Figure 1, it is observed that the elongation at break of unexposed PP/PA-6 blend increases significantly with increasing the PP-*g*-MA content up to 4 wt%, which represents a saturation level. Beyond this, the compatibilizer effect appears to be almost negligible. According to Zeng et al.,[2] the fracture under static tension of the uncompatibilized blends, occurs too early owing to the poor interfacial bonding and voids, which result in small elongation at break. Whereas, the increase of elongation at break of PP/PA-6 blends with the addition of PP-*g*-MA up to a saturation level is explained by the formation of PP-*g*-PA-6 copolymer, which

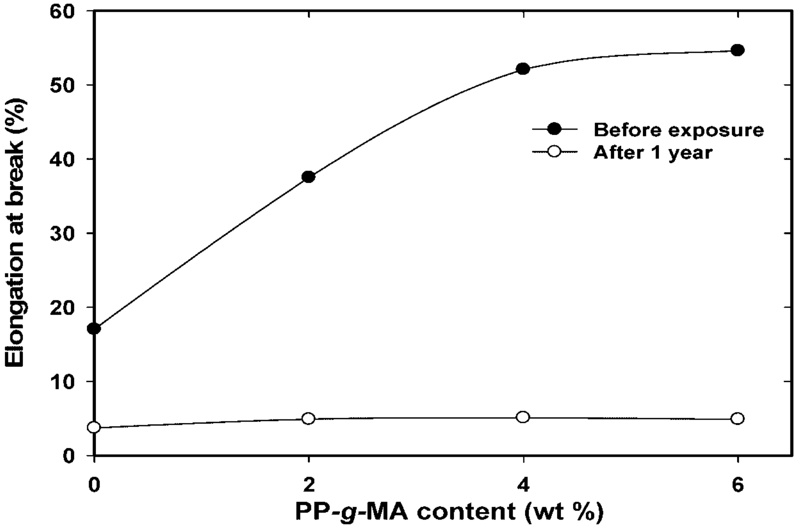

Figure 1.
Evolution of the percent elongation at break of PP/PA-6 blends as a function of PP-*g*-MA content before and after 1 year in natural weathering.

enhances the interface between the PP and PA-6 phases. Subsequently, the compatibilized PP/PA-6 blends could withstand the tensile deformation to higher elongation values.[11] Further, it is also reported by Sathe et al.[14] that up to a saturation level of the compatibilizer, its molecules are located at the interphase between the matrix and the dispersed phase. However, when the concentration of a compatibilizer is above the saturation level, only a part of the molecules locates in the interfacial area, and the excess is dispersed in the matrix affecting its homogeneity and consequently the mechanical properties of the blends. After 1 year of exposure, the values of elongation at break of PP/PA-6 blend decreases markedly, independently on the compatibilizer content ratio. At this aging level, all the irradiated materials are very brittle. The results are consistent with the morphological data indicating the micro cracks and holes on the fractured surfaces of the irradiated blends. Figure 2 shows the variation of the stress at break of PP/PA-6 blends as a function of PP-*g*-MA content before and after 1 year of exposure. It can be observed that there is a substantial increase in the stress at break of the PP/PA-6 blend with the addition of compatibilizer as a result of the improved interfacial adhesion between PP and PA-6, thus affecting the morphology of the blends.[15] After 1 year, both uncompatibilized and compatibilized blends show a large decrease in the stress at break values by more than 60%. However, the values of stress at break are almost the same for all the studied blends.

SEM Analysis

Figure 3(a) and (b) shows SEM micrographs of fracture surface of PP/PA-6 blends before and after 1 year in natural weathering, respectively. From Figure 3(a), it is observed that the morphology exhibits irregularly shaped and large domains of PA-6 dispersed in PP matrix ranging from 1 to 50 μm diameters. Moreover, the domains are easily detached from the PP matrix due to the poor interfacial adhesion between them. Furthermore, some voids of various sizes are visible on the surface.

The lack of plastic deformation on the fracture plane explains the sharp drop in the ductility of the PP/PA-6 blends.[16] After 1 year of outdoor exposure as shown in Figure 3(b), the morphology of PP/PA-6

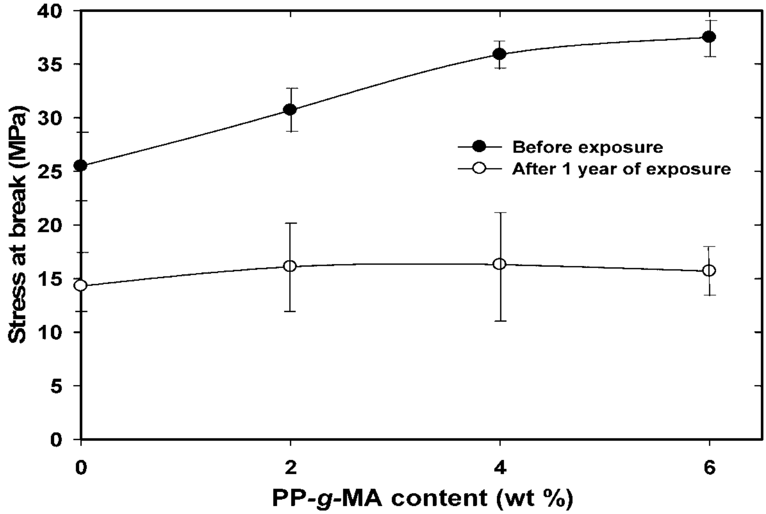

Figure 2.
Evolution of the stress at break of PP/PA-6 blends as a function of PP-*g*-MA content before and after 1 year of exposure in natural weathering.

blend is not so different from the reference one as characterized by the presence of agglomerates of larger size on the fracture surface. The damage caused by natural weathering on the morphology of PP/PA-6 blend is not well evident through SEM observations due probably to the presence of a great number of surface irregularities (surface roughness, holes, cracks, craters, aggregates, etc.) in the unexposed blend, characteristics of incompatible blends. Whereas, it can be noticed in Figure 4(a), which is relative to unexposed compatibilized PP/PA-6 blend, homogeneous phase structures in which the PA-6 particles are embedded in the matrix. The addition of 2 wt% of PP-*g*-MA, taken as example, has significantly increased the dispersion and particle size distribution of the PA-6 within the PP matrix. The improved morphology of PP/PA-6/2C results probably from the formation of an interfacial copolymer.[13] After 1 year of exposure (see Figure 4(b)), the morphology of the compatibilized PP/PA-6 blend shows the formation of many voids and cracks as a result of photo-oxidative degradation.

Conclusion

This work studied the effects of natural weathering for 1 year on properties of

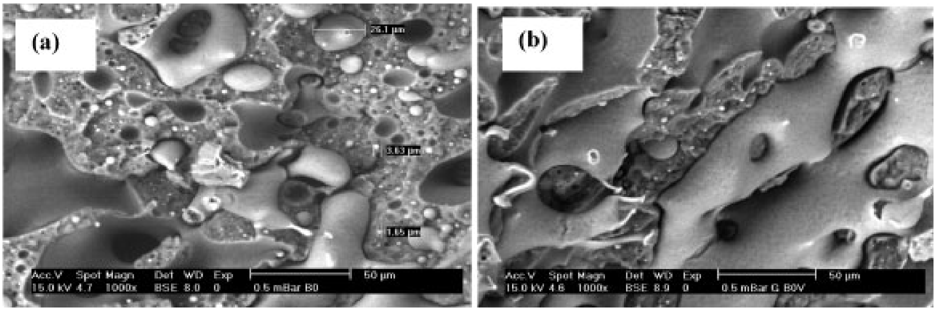

Figure 3.
SEM micrographs of PP/PA6/0C. (a): before exposure and (b): after 1 year in natural weathering. 1000X.

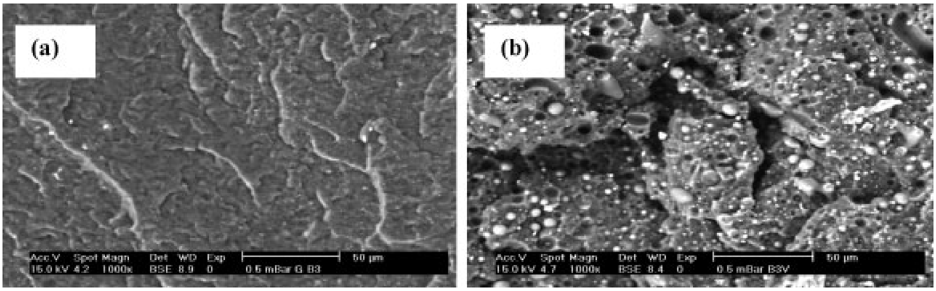

Figure 4.
SEM micrographs of PP/PA6/2C blends. (a): before exposure and (b): after 1 year in natural weathering. 1000X.

blends based on PP/PA-6: 70/30 wt % in the absence and presence of PP-*g*-MA. Through FT-IR analysis, no important changes in the chemical structure are observed for both uncompatibilized and compatibilized blends. Further, the addition of PP-*g*-MA had no effect on the degradation process. However, the exposed blends of PP/PA-6 whether compatibilized or not, become brittle as indicated by a large decrease in elongation at break and the formation of many voids ands cracks on the fracture surface as a result of weathering degradation.

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