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The Effects of long time exposure to Natural Weather on the Rheological and Morphological Properties of Polypropylene/Polyamide-6 Blends

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ABSTRACT

The effects of natural weathering exposure for a period of one year on the properties of polypropylene (PP)/polyamide-6 (PA6): (70/30 wt %) blends have been investigated in the absence and the presence of PP-*g*-MA used as a compatibilizer . The resulted changes in morphology and rheological properties of the different blends were studied by means of scanning electron microscopy (SEM), melt flow index test (MFI) and rheometry. After one year of natural weathering exposure, the results showed a significant increase of MFI values all the samples. The rheological measurements indicated a decrease in the complex viscosity of PP, PA6 and their blends as a result of chain scission mechanism; however, the decrease was more pronounced by the addition of the compatibilizer at this stage of time exposure. Further, the weathering effect on the morphology of exposed PP/PA6 observed by SEM revealed the presence of voids and cracks on the fractured surfaces for both virgin and compatibilized blends.

Key words: *PP, PA6, polymer blends, natural weathering, degradation.*

I. Introduction

In the last years, polymer blends have gained much interest because of the favourable balance of properties and cost [1]. Blending is mainly used to achieve properties, witch are more advantageous than those of the components [2]. Polymer blends based on polypropylene (PP) and polyamide 6 (PA6) are of great interest owing to their excellent mutually compensating properties [3]. PP is a commodity polymer witch offers a good barrier to moisture, a great chemical resistance and high impact strength with a low cost. On the other hand, PA6 is an excellent engineering plastic with good abrasion resistance and electrical properties. However, it has a high cost and a considerable water sorption [1]. Unfortunately, the two polymers are immiscible and blending them leads to macro-phase separation and consequently to a material of poor properties [4]. The miscibility of the two components may be improved by the addition of a compatibilizer. Many investigations have been carried out of PP/PA6 blends with grafted polymers and copolymers as compatibilizers. Among these compatibilizers the maleic anhydride grafted polypropylene PP-g-MAH showed appreciable results [5].

In outdoor applications, all polymers degrade. The extent of the degradation depends mostly on the environment (especially sunlight intensity, temperature, humidity, rain, wind, etc) and the polymer structure. In the presence of air and by the action of light, photo oxidation is believed to be the most important degradation process [6].

Many studies shown that ultraviolet (UV) photo degradation follows four different steps starting with free radical chain initiation, propagation, chain branching and termination.

Chemical degradation of polymers is an irreversible change and is very important phenomenon, which affects their performances in daily life and leads finally to the loss of functionality. [7]. Thus, the study of degradation and stabilization of polymers is extremely important from the scientific and the industrial point of view, to insure a long service light of the product.

Long-term properties of polymer blends under environmental stresses are influenced by degradation conditions, structures of components and by co-reactivity between individual component polymers and/or their degradation products that may lead to new chemical species such as grafted copolymers. Individual component of a blend may behave rather differently from their behaviour as isolated polymers [1, 2]. This may affect the degradation resistance of a blend positively or negatively. Extensive work has been devoted on the elaboration and characterisation of PP/PA6 blends [3,4]. Nevertheless, only very papers deal with their ageing, and more particularly with the ultraviolet (UV) photo degradation in the presence of a compatibilizer. Photodegradation behaviour of polypropylene/polystyrene blends compatibilized with styrene-butadiene-styrene (SBS) has been studied [8]. The results showed that compatibilizer influences the kinetics and the carbonyl content generated during the blend

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degradation, resulting in increased the photodegradation rate.

The aim of the present work was to investigate the long time exposure to natural weathering effect on the rheological and morphological properties of PP/PA6 blends compatibilized with the maleic anhydride grafted polypropylene (PP-g-MA). The kinetics of degradation were not studied. The degradation of the exposed samples is evaluated MFI test, Rheometry and SEM.

II. Materials and Methods

II.1.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 (MFI) = 3 g/10 min (at 230 °C and 2.16 kg), a melting point = 163°C and a Vicat softening point = 156°C.

PA6 was supplied by Lanxess (Germany) under the trade name Durethan B 30 S**.** PA6 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 (MFI) of 120 g/10 min, a melting temperature of 162 °C and a decomposition temperature higher than 250 °C.

II.2.Samples preparation

Melt compounding of PP/PA6 blends was performed on a Bauzano Counter rotating twin screw extruder (Italy) with a ratio L/D = 19. The temperature setting along the zones of the extruder was 240 °C, whereas the screw rotational speed was 40 rpm. Prior to extrusion, PA6 pellets were dehumidified in a Moton MDE 40 Desiccant dryer at 90°C for 3 hours. All the blend components, i.e. PP, PA6 and PP-*g*-MA were premixed together before addition to the hopper of the extruder according to the compositions reported in Table I. 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, PA6 and all the blend materials were dried at 90°C for 3 hours.

TABLE I
CODE AND COMPOSITION OF THE SAMPLES

Code	*PP(wt%)*	*PA6(wt%)*	*PP-g-MA (wt%)*
PP	**100**	**0**	**0**
PA6	**0**	**100**	**0**
PP/PA6/0C	**70**	**30**	**0**
PP/PA6/2C	**68**	**30**	**2**

II .3. Natural weathering exposure

Natural weathering of PP/PA6 blend samples was carried out according to ASTM D 1435. The specimens were mounted 45°, facing the south direction. 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 Jun 2009. The average radiation in the experimental period was 400 kcal/cm^2 per 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.

2.4. Characterisation methods

The melt flow index of PP/PA6 blends before and after exposure to natural weathering was measured using a Davenport MFI-10 melt flow indexer -Lloyd Instruments (England) at 240 °C and 2.16 kg load. The melt flow rate test is a simple and convenient method for characterizing both the type of degradation (chain scission or cross-linking) and the extent of degradation of a polymer since the melt flow index (MFI) is inversely related to the molar mass of the polymer.

The rheological properties of the samples before an after exposure to natural weathering were studied using a strain-controlled ARES rheometer (TA Instruments, Delaware, USA) under nitrogen atmosphere to prevent oxidative degradation. Specimens for shear rheological testing were prepared by moulding discs, about 1 mm thick, designed to match the platen diameter employed in the rheometer. Parallel plates of 25 mm diameter for the dynamic tests were used at T=240 °C. Prior forming the specimens and testing, all the blends were dried under vacuum at 90 °C for 3 hours.

The effect of natural weathering on the morphology of PP/PA6 blends was observed with a Philips XL30 Scanning electron microscopy (SEM) operated at 15 kV. SEM micrographs were taken from fractured surfaces of samples after submersion in liquid nitrogen.

III. Results and Discussion

III.1.Melt flow index (MFI)

The variation of MFI values of PP/PA6 blend is shown in Table 2 before and after 1 year of exposure to natural weathering. It is observed that the MFI of PP/PA6 blends is comprised between those of the two components PP and PA6. It is also observed a large decrease of the MFI values of PP/PA6 blend after addition of 2 wt % of PP-*g*-MA before slowing down at higher compatibilizer content. According to the literature [9] the use of PP-*g*-MA as compatibilizer in PP/PA6 blends may result in a physical interaction with PP and a chemical interaction with PA6. The anhydride group of maleic anhydride would react with amine end-groups of PA6 with formation of an imidic linkage; the reaction leads to creation of PA6-*g*-PP copolymer. The intermolecular bonding in the copolymer may restrict the mobility of the molecular chains in the PP/PA6 blends, thus decreasing the MFI values. After 1 year of exposure, it is clearly observed a fast increase in the MFI values of all the samples. These results indicate the degradation of the samples under UV light by chain scission mechanism, leading to improvement of mobility of the molecular chains, thus increasing the MFI.

TABLE II
MELT FLOW INDEX (MFI) OF THE SAMPLES BEFORE AND AFTER 1 YEAR OF EXPOSURE TO NATURAL WEATHER.

Samples		*MFI (g/10mn)*	*Dimensionless MFI*
PP	**Before exposure**	**3.21**	**0.12**
	After exposure	**25.7**	
PA6	**Before exposure**	**27.3**	**0.42**
	After exposure	**63.9**	
PP/PA6/0C	**Before exposure**	**12.3**	**0.34**
	After exposure	**35.9**	
PP/PA6/2C	**Before exposure**	**8.88**	**0.28**
	After exposure	**30.77**	

Furthermore, table II shows the dimensionless MFI of all the investigated samples. The dimensionless values were calculates as the MFI value before exposure to natural weather divided by the @corresponding value after 1 year of exposure to natural weather. It can be seen that the dimensionless MFI value of PA6 is higher than that of PP by almost 350 %, passing from 0.42 to 0.12 respectively. This means that the extent of degradation of PP is more important than that of PA6. It can be also seen that the dimensionless MFI value of compatibilized PP/PA6 blends is less than that of the uncompatibilized blends. This result suggests that the compatibilizer agent (PP-g-MA) acts as a chain scission promoter at this stage of time exposure.

III.2. Rheological measurements

The curves of complex viscosity (η*) and storage modulus (G') versus frequency for PP and PA6 before and after 1 year of exposure in natural weathering are shown in Fig. 1(a) and (b) respectively. It is observed that all the curves in Fig. 1.a show almost the same pattern which is characterized by a regular increase of η* with decreasing the frequencies. It is also noted a large drop of η* of PP and PA6 after exposure to natural weather. This indicates that molecular chain scission is dominant under UV light. The drop of η* is more pronounced in the case of P, meaning that the extent of degradation of PP is higher than that of PA6. These results seem to be consistent with the MFI results. The storage modulus (G') resulting from the dynamic frequency scans are shown in Fig. 1.b. It is observed that (G') of both PP and PA6 decreases with decreasing the frequencies. The decrease is more important in the case of PP, witch undergoes with the η* results. It should be mentioned that the slow decrease of (G') of PA6 in the range of 1 - 0.1 rad/s is due to the very low values of torque (<10^{-6} N.m) in this range.

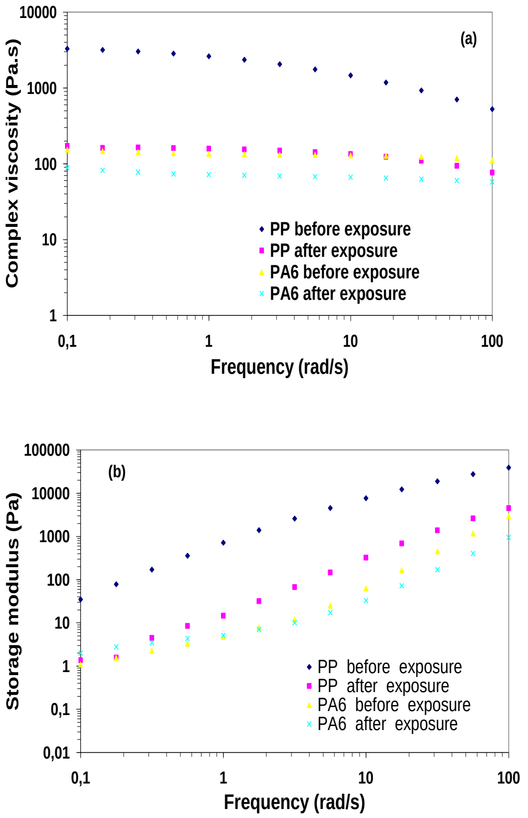

Fig. 1 Complex viscosity (a) and Storage modulus (b) of PP and PA6 as a function of frequency at 240°C before and after 1 year of exposure to natural weather.

The curves of complex viscosity (η*) and storage modulus (G') versus frequency for PP/PA6 blends in the absence and presence of PP-*g*-MA (2 wt %) before and after 1 year of exposure in natural weathering are exhibited in Fig. 2(a) and (b) respectively. It is observed that addition of 2 % PP-g-MA increases considerably the viscosity of PP/PA6 blend, especially at 0.1 Hz (Fig. 2a), clearly indicating an enhanced interaction between the two polymer phases due to the formation of copolymers by interfacial reactions in the melt. The chemical compatibilization reaction is expected to take place between the anhydride or carboxyl groups of the functionalized PP and the amine groups of the polyamide as reported by many authors [10].

Similar conclusions may be drawn from the curves of G' (Fig. 2b), where the addition of the compatibilizer increases the storage modulus of PP/PA6 blends. This may be explained as a result of the PP-*g*-MA effect leading to improvement of miscibility of the blends, and thus to better dispersion of PA6 in PP matrix. Further, the decrease in complex viscosity of the whole irradiated blends indicates that chain scission is dominant in natural weathering. Moreover, the drop of η* is more pronounced after the addition of PP-g-MA, meaning that the compatibilizer acts as chain scission promoter at this stage of time exposure. These results seem to be consistent with the MFI results.

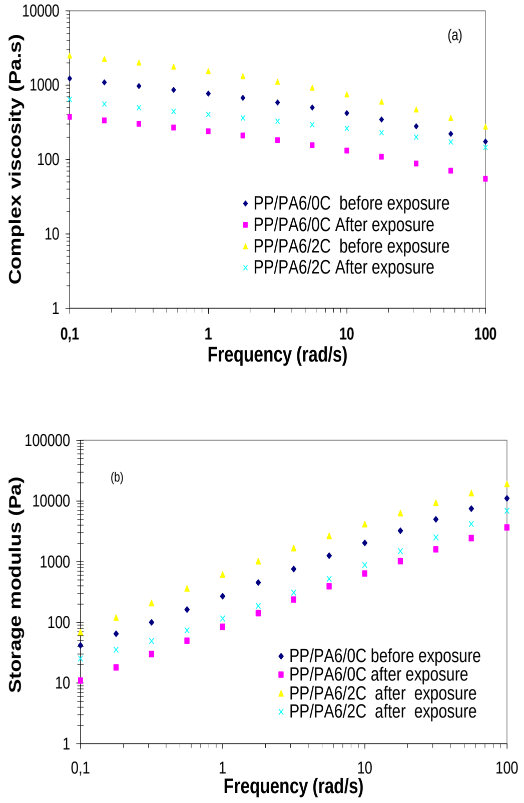

Fig. 2 Complex viscosity (a) and Storage modulus (b) of PP/PA6/0C and PP/PA6/2C as a function of frequency at 240°C before and after 1 year of exposure to natural weather.

III.3. SEM analysis

SEM is a powerful tool to investigate the phase morphology of the polymer blends and particularly, the possibility of evaluating the interfacial modification in the presence of compatibilizers, the dispersion of the phases and the reciprocal adhesion [30]. In this respect, Fig. 3a and b shows SEM micrographs of cryo-fractured surfaces of PP/PA6: 70/30 blend before and after 1 year of exposure in natural weathering, respectively. From Fig. 3a, it can be observed that the morphology exhibits irregularly shaped and large domains of PA6 dispersed in PP matrix ranging from 2 to 34 µm in diameter. Moreover, the domains are easily detached from the PP matrix due to the poor interfacial adhesion between them. Further, some voids of various sizes are visible on the surface. Similar results have been reported in literature [10]. The lack of plastic deformation on the fracture plane explains the sharp drop in the ductility of the PP/PA6 blend. After 1 year of exposure as shown in Fig. 3b, a great damage on the morphology of PP/PA6 blend is observed owing to photooxydative degradation.

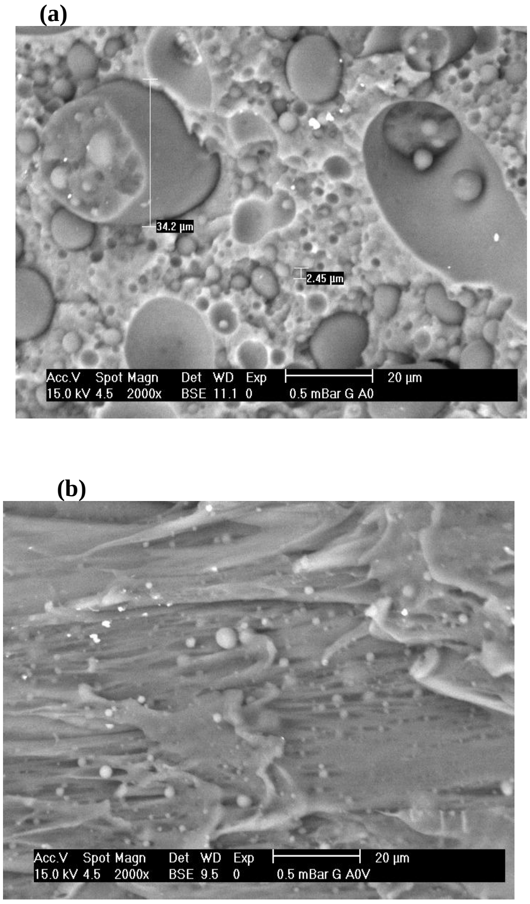

Fig. 3 SEM micrographs of PP/PA6:/0C. (a): before exposure and (b): after exposure. 2000X.

On the other hand, it can be noticed in Fig. 4a, which is relative to unexposed compatibilized

PP/PA6 blend, homogeneous phase structures in which the PA6 particles are embedded with the PP matrix. As expected, the addition of 2 wt % of compatibilizer, taken as example, has significantly increased the dispersion and particle size distribution of the PA6 within the PP. PP-*g*-MA provides a good wetting of PA6 leading to improved adhesion to the PP matrix creating a blend with improved impact properties versus polypropylene homopolymer while maintaining or improving strength . As suggested by Roeder et al. [11], the improved morphology of PP/PA6/PP-*g*-MA results from the formation of an interfacial copolymer.

After 1 year, similar comments can be made for the aged sample as shown in Fig. 4b. Many voids and cracks are observed with however, a good distribution of the dispersed phase in the PP matrix. Furthermore, the incorporation of PP-*g*-MA in PP/PA6 blend leads to a finer dispersion of the PA6 domains. The presence of voids and cracks in the exposed sample indicates the occurrence of photooxydative degradation.

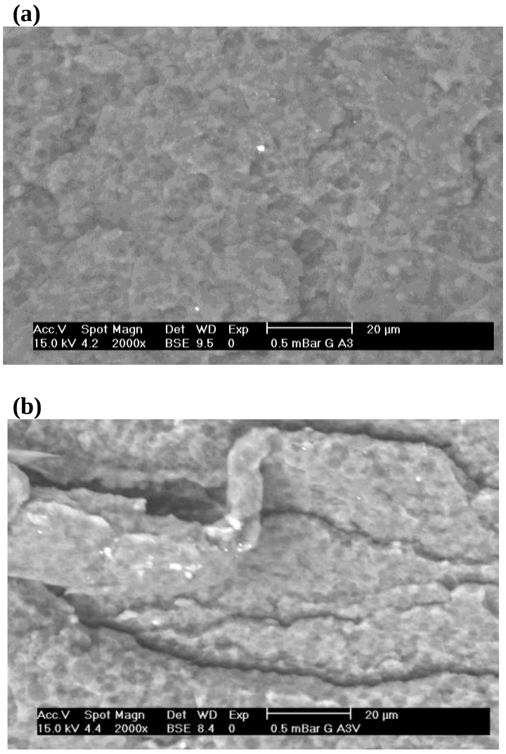

Fig. 4 SEM micrographs of PP/PA6/2C (a): before exposure and (b): after exposure. 2000X.

On the other hand, it can be noticed in Fig. 4a, which is relative to unexposed compatibilized PP/PA6 blend, homogeneous phase structures in which the PA6 particles are embedded with the PP matrix. As expected, the addition of 2 wt % of compatibilizer, taken as example, has significantly increased the dispersion and particle size distribution of the PA6 within the PP. PP-*g*-MA provides a good wetting of PA6 leading to improved adhesion to the PP matrix creating a blend with improved impact properties versus polypropylene homopolymer while maintaining or improving strength . As suggested by Roeder et al. [11], the improved morphology of PP/PA6/PP-*g*-MA results from the formation of an interfacial copolymer. After 1 year, similar comments can be made for the aged sample as shown in Fig. 4b, except that the damage on the morphology of the compatibilized PP/PA6 blend is more important compared to the uncompatibilized blend. Many voids and cracks are observed with however, a good distribution of the dispersed phase in the PP matrix. Furthermore, the incorporation of PP-*g*-MA in PP/PA6 blend leads to a finer dispersion of the PA6 domains. The presence of voids and cracks in the exposed sample indicates the occurrence of photooxydative degradation.

IV. Conclusion

Based on this work devoted to study the effects of natural weathering exposure for one year on the properties of PP/PA6: 70/30 wt% blends in the absence and the presence of PP-*g*-MA, the following conclusions can be drawn:

Before exposure to natural weather, the results of melt flow index (MFI), complex viscosity (η*) and storage modulus (G') indicated that the addition of 2 (wt %) of PP-g-MA improves the compatibility of PP/PA6 blends, and consequently their rheologiacal and morphological properties.

After one year of exposure to natural weather, the (MFI) and (η*) of PP, PA6, compatibilized and uncompatibilized PP/PA6 blends increased drastically, indicating that chain scission is dominant in natural weather. Moreover, the complex viscosity and storage modulus of all the samples decreased drastically, witch is consistent with the MFI results. Furthermore, the results of MFI and (η*) indicate that the addition of PP-g-MA increases the extent of degradation of the blends after one year of exposure, meaning that the compatibilizer acts a chain scission promoter at this stage of time exposure.

The effects of natural weather on the morphology of PP/PA6 blends is characterized by the presence of many voids ands cracks on the fractured surfaces as a result of excessive degradation, which is in agreement with rheological data.

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