DOI: 10.1002/masy.201251115

Morphology and Properties of Polyamide 6/ Poly(propylene) Blends Fine-Tuned with Nanosilica

*F. Laoutid, D. François, Y. Paint, L. Bonnaud, P. Dubois**

Summary: The influence of the incorporation of hydrophobic nanosilica on morphological and mechanical properties of polyamide 6 (PA) and poly(propylene) (PP) blends has been investigated. Depending on the amount of silica nanoparticles in the blend and the melt mixing procedure, a strong refinement of PP (as minor dispersed phase) droplet size can be achieved thanks to the interfacial confinement of nanoparticles. The accumulation of nanoparticles at the interface allows the formation of an anti-coalescence rigid barrier around PP domains that prevents/refrains dispersed phase domains from coalescence as highlighted by transmission and scanning electron microscopies. The mechanical properties of the hybrid blends were also discussed and interpreted in relation with the blend morphology.

Keywords: blends; compatibilization; nanocomposite; polyamide; poly(propylene)

Introduction

The compatibilization of immiscible polymer blends is an efficient way that allows for the development of new materials, with modulated properties, from existing polymers. In fact, in most cases, thermodynamics does not support intimate polymer mixing and the resulting alloys generally exhibit poor mechanical properties. Compatibilizing agents such as block copolymers or functionalized polymers, that present a chemical affinity with the two phases, are the most used to improve the performances of polymer blends by decreasing the interfacial tension between the two immiscible polymeric phases and by promoting some stress transfer between the two phases.

Recently, various studies have highlighted the interest of using nanofillers, [1–5] as interfacial/“compatibilizing” agents for immiscible polymer blends. They could form a rigid barrier, under certain conditions, [6,7] that prevents coalescence and thus reduces the size of the dispersed phase.

The main objective of this study consists in using pyrogenic nanosilica to stabilize PA/PP (80/20; wt/wt) blend morphology since this kind of blend could present an interesting combination of both PP and PA inherent properties, i.e., polyamide phase can provide good thermal properties while PP can ensure good processability and resistance to moisture.

Experimental Part

Materials

The polymers used in this study are commercial products: polyamide 6 (PA) from DSM Engineering Plastics (Akulon F136-c1, MFI at 240 °C and 2.16 kg = 5.75 g/10min) and poly(propylene) homopolymer (PP) from Polychim, (B 10 FB, MFI at 240 °C and 2.16 kg = 15.6 g/10min). CAB-O-SIL® TS530 (225 m^2/g) is hydrophobic fumed silica, treated with hexamethyldisilazane and characterized by an average particle (aggregate) length of ca. 200–300 nanometer.

Center of Innovation and Research in Materials & Polymers (CIRMAP), Laboratory of Polymeric and Composite Materials (LPCM), University of Mons UMONS & Materia Nova Research Center, Place du Parc 20, 7000 Mons, Belgium
E-mail: philippe.dubois@umons.ac.be

Processing

Before processing by melt-blending, PA and nanosilica were dried overnight at 80 °C under vacuum. Polyamide/polypropylene blends were prepared by using a vertical co-rotating twin-screw DSM mini-extruder (capacity 15cc) in two steps at 240 °C. PA and silica nanoparticles were first mixed for 2 minutes at 30 rpm, and then PP was introduced in the micro-extruder for further 4 (but also 9, 14) minutes mixing at 100 rpm. One-step mixing in which the three components were simultaneously introduced in the extruder was also carried out. A Thermo-Haake mini-injection machine was used to produce specimens for tensile testing (type ISO ½ - 1BA with thickness of 1.5 mm x 60 mm × 10 mm) as follows: temperature of the barrel: 260 °C; time for preheating and melting: 120 seconds; temperature of the mold: 60 °C. The compositions of the prepared blends are presented in Table 1.

Morphological Characterization

Scanning electron microscopy (SEM) analysis was performed by using a JEOL JSM 6100 apparatus at 10 kV and transmission electron microscopy (TEM) micrographs analyses were performed with a Philips CM100 apparatus using an acceleration voltage of 100 kV. The specimens were previously prepared by ultra-cryo-microtomy cutting (Leica Ultracut) starting from injection molded samples.

Mechanical Analysis

Tensile testing measurements were performed by using a Lloyd LR 10 K tensile bench at a speed rate of 10 mm/min using a distance of 58 mm between grips. All mechanical tests were carried out by using specimens previously conditioned for at least 48 h at 20 ± 2 °C under a relative humidity of 50 ± 3% and the values were averaged out over 6 measurements.

Table 1.
Content (expressed in wt%) in PA, PP and silica nanoparticles used for the preparation of polymer blends.

Composition	PA	PP	SiO_2
PA-PP (80–20)	80	20	—
PA-PP (80–20) - 1% TS530	79.2	19.8	1
PA-PP (80–20) - 3% TS530	77.6	19.4	3
PA-PP (80–20) - 5% TS530	76	19	5

Results and Discussion

The mixture of polyamide and polypropylene leads to the formation of heterogeneous structure (Figure 1) containing irregular PP domains resulting from the competition between the deformation/break-up of the dispersed PP phase and the coalescence of so-formed nodules. The addition of 5 wt% of hydrophobic silica to the PA/PP (80/20; wt/wt) blends triggers strong refinement of the size of the dispersed phase thanks to the location of nanosilica at the interface between PA and PP phases (Figure 2). The accumulation of nanosilica at the interface leads to the formation of a rigid barrier around minor PP phase that prevents coalescence of PP domains and favours only dispersed phase break-up.

Indeed, the size of PP dispersed domains remains remarkably stable over time and does not change even if the mixing time in the extruder is largely increased (Figure 3). Such morphology and domain size remaining constant whatever the applied mixing time attest for stable PA/PP/nanosilica formulations mainly driven by thermodynamics rather than kinetic criterions.

The mechanical properties of PA/PP (80/20; wt/wt) blend and related nanocomposites have been determined by tensile testing. The recorded values of Young modulus, stress at yield and strain at break are gathered in Table 2 and compared to the pristine PA and PP polymers. As expected, the addition of 20 wt% of PP reduces the tensile modulus, the stress at yield and strain at break of PA indicating poor adhesion between immiscible PA and PP phases. The addition of 5 wt% of silica nanoparticles to the same blend triggers a significant increase of Young Modulus, stress at yield and an important improve-

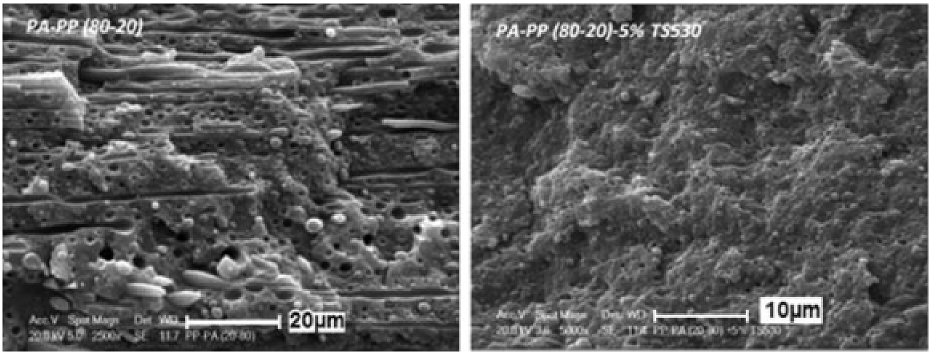

Figure 1.
Effect of silica nanoparticles on PA/PP (80–20; wt/wt) blends morphology; left: unfilled blend; right: blend filled with 5 wt% of silica nanoparticles.

ment of the strain at break (up to 116%). However, the stress at yield remains lower than that of pristine PA since silica nanoparticles do not improve the interfacial adhesion between PA and PP. Indeed, hydrophobic silica nanoparticles being simply covered by unreactive trimethylsilyl groups no specific interactions could be established between the polymer chains and the nanofiller surface.

The anti-coalescence action of silica depends strongly on its content in the blend as shown by SEM observations of PA/PP blends containing different amount of nanoparticles (Figure 4). In fact, at lower silica content (from 3 to 1 wt%), the blend morphology becomes more and more chaotic, irregular with much larger PP domains.

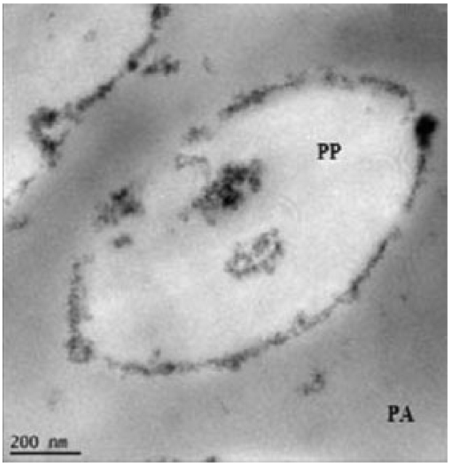

Figure 2.
TEM images of PA/PP (80/20; wt/wt) filled with 5 wt% hydrophobic silica.

The change of the blend morphology affects dramatically the elongation at break which decreases as the amount of hydrophobic silica content is diminished (Table 2) supporting good correlation between the size of PP dispersed domains and the elongation at break of the formed blend.

The ductility of these PA/PP-based nanocomposites decreases with increasing the amount of PP in the blend (Figure 5). For PP content above 40 wt%, the nanocomposites display a brittle behaviour with very low values for the elongation at break while for PP content below 40 wt%, the resulting material remains ductile and the effect of the size reduction of PP nodules continues to act positively on the mechanical properties. In this last case, mixing simultaneously all constituents, i.e. so-called "one-step" blending in Figure 5, leads to a dramatic decreasing of the elongation at break especially when the blend contains 20 wt% of PP.

When the mixing is performed in one step, the anti-coalescence action of silica seems to be reduced because silica nanoparticles are first located into dispersed

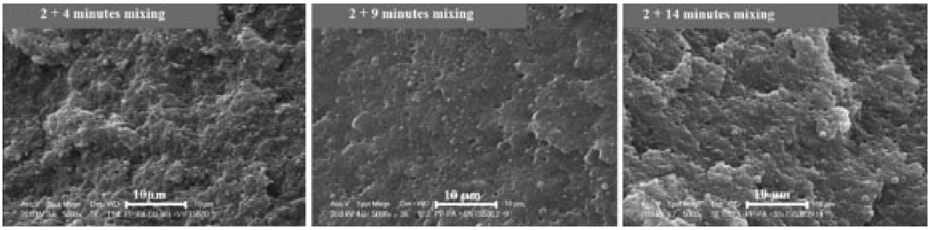

Figure 3.
SEM images of PA/PP (80–20) blends filled with 5 wt% hydrophobic silica nanoparticles and mixed for extra 4, 9 and 14 minutes after introduction of PP phase.

Table 2.
Mechanical properties of PA, PP and the corresponding blends.

	Young Modulus (MPa)	Stress at Yield (MPa)	Elongation at break (%)
PA	2170 ± 90	80 ± 8	150 ± 27
PP	1490 ± 160	32 ± 2	390 ± 70
PA – PP (80–20)	1700 ± 100	38 ± 3	38 ± 10
PA – PP (80–20)- 1% SiO_2	2000 ± 160	53 ± 2	8 ± 2.5
PA – PP (80–20)- 3% SiO_2	2300 ± 80	56 ± 1.5	25 ± 5
PA – PP (80–20)- 5% SiO_2	2170 ± 120	51 ± 3	116 ± 14

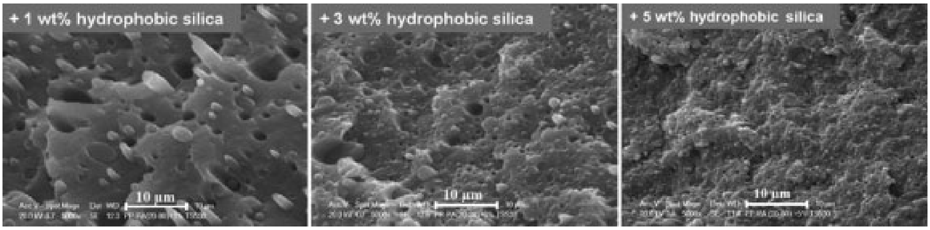

Figure 4.
TEM images of PA/PP (80/20; wt/wt) blends filled with 1, 3 and 5 wt% of hydrophobic silica nanoparticles.

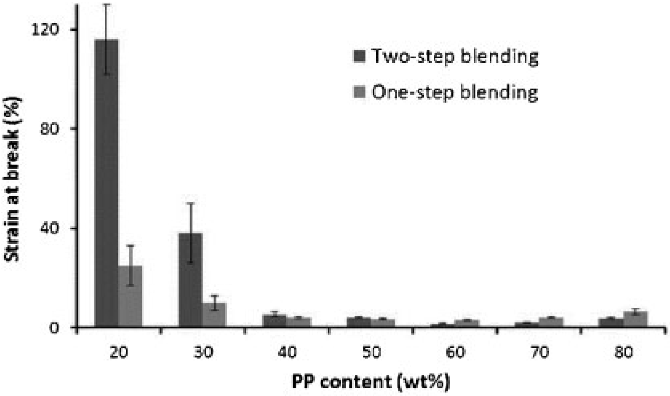

Figure 5.
Effect of PP content and blending procedure on strain at break of PP/PA blends filled with 5 wt% silica nanoparticles.

polyolefinic phase since PP melts before PA.

Conclusion

The morphology and mechanical properties of PA/PP (80/20; wt/wt) blend filled with pyrogenic nanosilica have been investigated. The silica confinement at the interface between the two polymers allows the formation of a rigid anti-coalescence barrier that prevents/refrains dispersed phase domains from coalescence and leads to an important size reduction of the dispersed PP phase domains. Indeed, we observed that increasing extrusion time does not modify the blend morphology, which remains stable. Nevertheless, to achieve a good morphology control, at least 5 wt% of hydrophobic silica is needed. The mixing procedure also appears to be a key-parameter that contributes to the morphology formation. The control over coalescence allows a morphology refinement of the blends, which seems to be sufficient to achieve good mechanical properties for blends containing 20 wt% of PP content.

Acknowledgements: Authors thank Wallonia Region, Nord-Pas de Calais Region and European Community for the financial support in the frame of the IINTERREG IV – NAVARE project. This work was also supported by the European Commission and Région Wallonne FEDER program (Materia Nova) and OPTI^{2-}MAT program of excellence, by the Interuniversity Attraction Pole program of the Belgian Federal Science Policy Office (PAI 6/27) and by FNRS-FRFC.

[1] Q. Su, M. Feng, S. Zhang, J. Jiang, M. Yang, *Polym. Int.* **2007**, *56*, 50.
[2] S. Sinha Ray, M. Bousmina, *Macromol. Rapid. Commun.* **2005**, *26*, 450.
[3] O. Persenaire, J.-M. Raquez, L. Bonnaud, P. Dubois, *Macromol. Chem. Phys.* **2010**, *211*, 1433.
[4] L. Elias, F. Fenouillot, J. C. Majesté, P. Cassagnau, *Polymer* **2007**, *48*, 6029.
[5] L. Wenjing, J. Karger-Kocsis, R. Thomann, *J. Polym. Sci. Pol. Phys.* **2009**, *47*, 1616.
[6] L. Elias, F. Fenouillot, J.-C. Majesté, G. Martin, P. Cassagnau, *J. Polym. Sci. Pol. Phys.* **2008**, *46*, 1976.
[7] F. Fenouillot, P. Cassagnau, J.-C. Majesté, *Polymer* **2009**, *50*, 1333.