

## Morphology and properties of isotactic polypropylene/polystyrene in situ microfibrillar reinforced blend nanocomposite fibers

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**Abstract:** Polypropylene/polystyrene blends containing organically modified montmorillonite (organoclay) were prepared using a twin screw extruder followed by fiber spinning. The melt intercalation of PP/PS blend was carried out in the presence of a compatibilizer. The crystallization, morphology, thermal behaviors and mechanical properties of PP/PS/ organoclay blends nanocomposite fibers were investigated. The improved adhesion between phases and fine morphology of the dispersed phase contributed to the significant improvement in the properties of the final blend nanocomposite fibers. On the basis of this result, we described a general understanding of how the morphology is related to the final properties of organoclay-incorporated PP/PS blends. The degree of fractionated crystallization is dependent on the interface of PS droplets and surrounding medium which could be controlled by nucleating effect of organoclay and dispersed phase and surpassing chain motion by silicate layers.

**Keywords:** Polypropylene, Polystyrene, Blend nanocomposite, Organoclay, Morphology.

### Introduction

It is the common practice to make new polymer materials by blending or alloying different polymers. However, it is difficult to obtain good dispersion in polymer blends whose components are insoluble in each other, particularly for combinations non-polar polymer with polar polymer [1-3], therefore, the compatibilization is necessary for the immiscible polymer blends. The compatibilizers are a block or graft copolymers, which exhibit intermolecular attraction or chemical reactions with the blend components. Maleic anhydride-g- polypropylene (PP-g-MA) is an effective precursor of the reactive compatibilizer for PP and polar polymer blends [3].

The blends of polyolefin and engineering polymer are since the latter can improve the mechanical properties of the relatively weak partner. The usage of polypropylene as one of the phases in polymer blends

is widely favored due to its excellent processability and low cost [4-8]. In recent years, organic-inorganic nanocomposites have attracted great interest because of high potential for applications as functional materials [4].

One of the most promising composites system would be the hybrid based on organic polymers and layered silicates. Layered, silicates dispersed, in the polymer matrix in the form of layers of crystals about 1nm thick and with a lamellar aspect ratio of between 100 and 1000 [5, 6].

In this direction, some studies related to nanocomposites of the blends have been reported, especially for polypropylene/polyamide-6/organoclay blend nanocomposites [8].

The incorporation of inorganic solid particles has been used as a method to stabilize the blend morphology due to the compatibilization effect produced by the adsorption of the two polymers on the solid surface. Moreover, the inorganic particle also

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have been used in toughening polymer with the objective to introduce a beneficial enhancement of elastic properties in the blends in addition to improvements in toughness [9-12].

Recently several groups have shown that clays can effectively reduce the domain size of polymer blends and they can play a role as compatibilizer in various immiscible polymer blends. Most of them attributed this behavior to the ability of organoclay affecting both, the interfacial tension and the viscosity ratio, which were important factors in the determination of the size of dispersed phase during mixing [13,14]. The organoclay could act as a compatibilizer between the immiscible polymers. Yet the microscopy alone is not enough to conclude about the compatibilization role of the organoclay. Furthermore, as the above short summary indicates, there are three possible mechanism of organoclay compatibilization: (1) By the action of organic modifier (intercalant) miscible in both blend components, (2) By the solid- melt adsorption that results in free energy gains, and (3) by migration to the interphase and modifying the interfacial tension between the two phases.

To have better insight into the role of organoclay in polymeric blends, the immiscible polymer pairs and PP-g-MA were melt blended with organoclay. Moreover, in the preceding studies, the added organoclay to the various blends were rather high, therefore an increase in viscosity could be the reason for the reduction in domain sites [15].

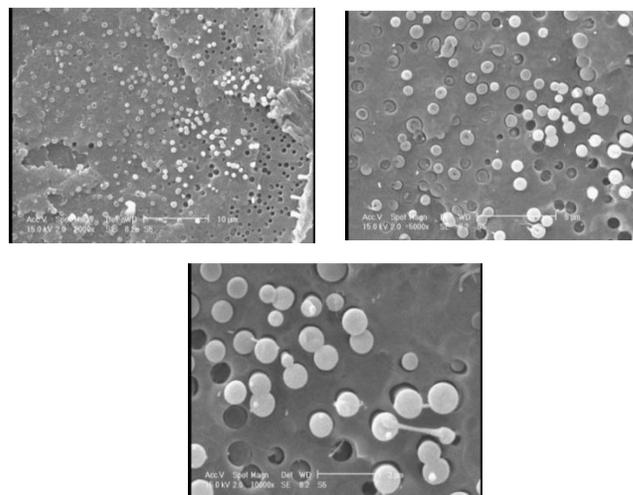
The main objective of this work was to address the fundamental question of compatibilization role of the organoclay and maleic anhydride grafted polypropylene (PP-MA) in immiscible polymer blend nanocomposite fibers to improve properties.

## Results and discussion

### Morphology of PS domain:

The SEM micrographs of PP/PS containing 1 wt% organoclay are shown in Figure 1. The white domains represent the position of the PS dispersed phase in the PP matrix. This could be explained by the fact that the polymer pairs of PP and PS are thermodynamically immiscible. As it can be seen in this picture the organoclay platelets prevent the coalescence of PS droplets and therefore consequently could promote droplet size reduction as the balance between break up and coalescence. The strain existed below the spinneret, which could deform the PS phase in fiber path. The specimens were analyzed at perpendicular direction to spinning flow (transverse/ direction) and

parallel to spinning flow (longitudinal direction). However, due to the complexity of flow in extruder, it is difficult to assert that the nature of the flow is responsible of the morphology obtained. To play this role, organoclay should be at least partially exfoliated and should have some interactions with both phases.



**Figure 1.** SEM micrographs of the 1% organoclay filled (79/15/5) PP/ PS / PP-g-MA blend nanocomposite fiber at three different magnifications.

### Thermal Analysis:

As it can be seen in Figure 2, DSC thermograms show two melting peaks indicating that PP matrix and PS dispersed phase show two different melting behaviors for all of samples in which lower melting point presents the PP characteristic peak.

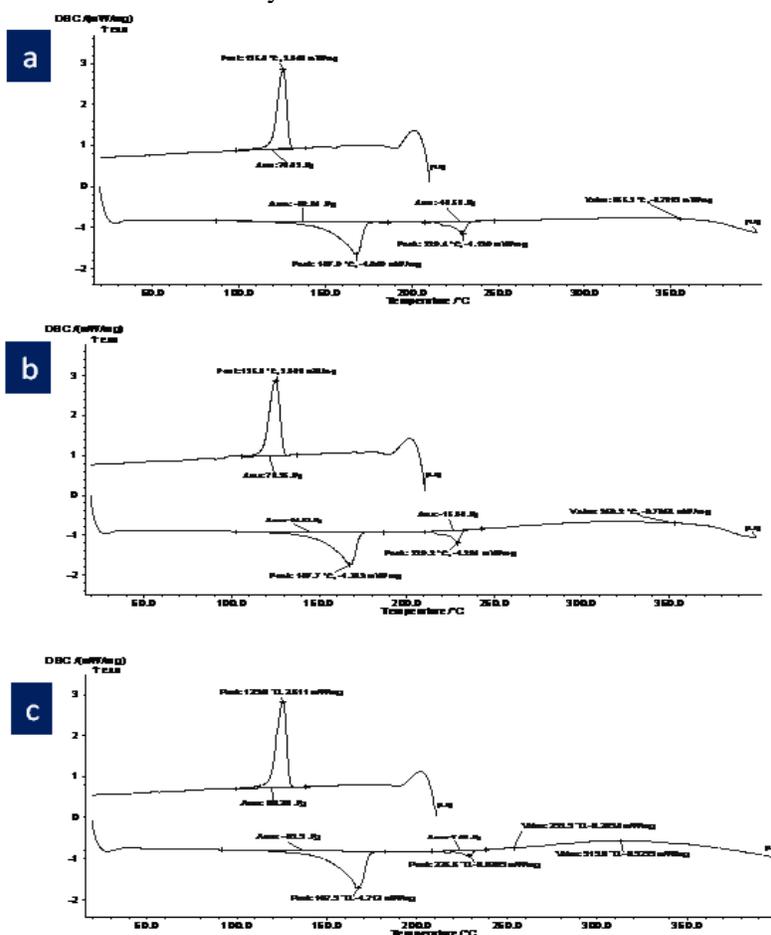
The thermal properties of samples also are presented in Table 1. Blending two polymers increases the crystallinity of PP as a result of nucleating effect of PS in the immiscible blend systems. By comparing these results it was found that incorporation of compatibilizer (samples 2 and 4) decreases the extent of crystallization of PS and increases the extent of crystallization of PP due to improve the fibrillation of PS. These results also indicated that the presence of organoclay decreases sharply the PS crystallinity as result of partitioning of higher amount of organoclay in the dispersed phase and decreases PP crystallinity by damaging effect of higher loading of organoclay on fibrillation process. The melting temperature  $T_m$  of PP did not appear to be different in the most polyblend and polyblend nanocomposite fibers in comparison to that of the neat PP fiber. The  $T_m$  of PS in polyblend and polyblend nanocomposite fibers, on the other hand, was consistently 2°C lower than the value of the corresponding neat fiber. Probably, the lower  $T_m$  of PS

in the fibers could be as a result of the formation of copolymer between PP-g-MAH and PS.

#### Wide angle x-ray diffraction analysis:

The wide angle X-ray diffraction patterns of polyblend and polyblend nanocomposite fibers are shown in Figure 4. There were no significant shifts in the diffraction positions of the two materials after forming the polyblend and polyblend nanocomposite fibers. This shows that the nature of the crystalline

lattices of the two materials did not undergo an appreciable change. The intensity of reflections at the angular positions  $2\theta$  of 14.2, 16.8 and 18.6 corresponding, respectively, to the 110, 040, and 130 planes of PP and  $2\theta$  of  $15^\circ$  corresponding to the 010 plane of PS actually increased. This suggests that each polymer component tended to enhance the size and perfection of the crystals of the other in the polyblend fibers.



**Figure 2:** DSC thermograms of (a) simple blend (Sample 4), (b) compatibilized blend (sample 2), compatibilized blend nanocomposite (Sample 7).

**Table 1.** DSC thermal properties and percent crystallinity for fibers.

Samples	T <sub>m</sub> of PP (°C)	T <sub>m</sub> of PS (°C)	Crystallinity PP (%)	Crystallinity PS (%)
PP	166.5	-	37.03	-
PS	-	231.3	-	23
2	167.7	229.2	56.56	20.56
3	167.4	229.3	59.07	16.27
4	167.9	229.4	50.38	22.58
5	166.9	228.5	46.98	14.03
7	167.3	228.8	39.08	8.65

#### Mechanical properties:

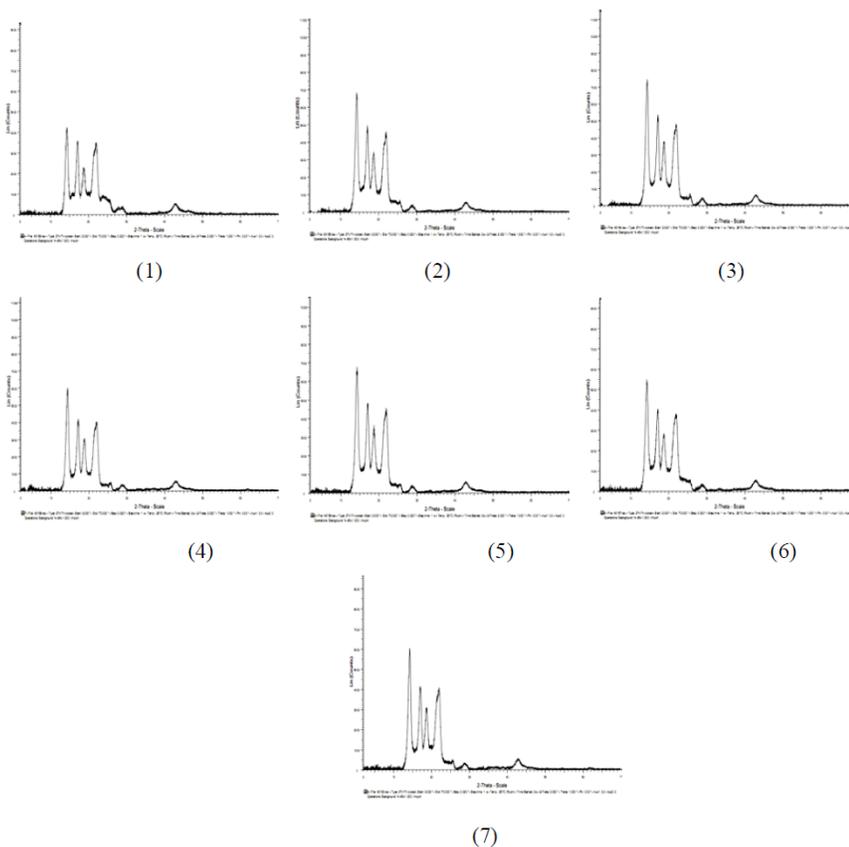
Tensile strength, modulus and elongation at break of different PP/PS blend fibers with and without organoclay and compatibilizer are listed in this Figure 4. The test results showed that the addition of PP-g-MA could improve the compatibilization of the PP/PS blends which was in favor of improving of mechanical properties therefore compatibilized blend fibers showed better properties even than that of pure PP fibers because of the formation of *in situ* micro PS fibrils. The PP/PS/PP-g-MA/organoclay blend nanocomposite fibers had better mechanical properties

than the blend fibers without organoclay. The tensile mechanical properties of the hybrid fibers were found to be increased with increasing organoclay content.

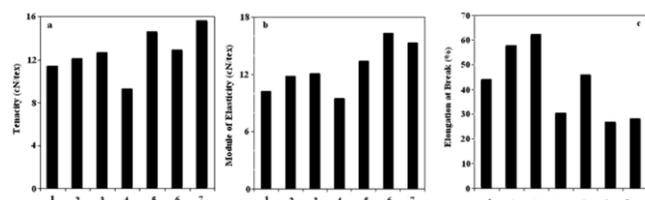
It was also found that presence of compatibilizer plays significant roles in determining the organoclay behavior and the extent of improvement of mechanical properties. This improvement in tensile strength and tensile modulus of the polyblend fibers containing

organoclay is thought to be dependent on the interactions between the polar polymer molecules and the layer organoclays, as well as on the rigidity of the clay layers themselves.

Indeed, the rigidity of the clay layers is considerably greater than the polymer molecules and thus they do not deform or relax to the same extent.



**Figure 3.** Wide angle X-ray diffraction spectra of samples.



**Figure 4.** Tensile properties of hybrid fibers.

## Conclusion

The effects of added of organically modified organoclay and PP-g-MA and different blend ratios on the morphology and properties of immiscible polypropylene polystyrene blend fibers were investigated. The results of this investigation indicated that the degree of fractionated crystallization is

dependent on the interface of PBT droplets and surrounding medium which could be controlled by nucleating effect of organoclay and dispersed phase and surpassing chain motion by silicate layers as these are influenced by location of organoclay in the phases. The compatibility of PP/PS blends can be dramatically improved with the addition of organoclay and PP-g-MA, which have excellent effect to reduce interfacial tension. PS dispersed phase likes organoclay serving as heterogeneous nucleation agent could benefit the crystallization of PP. The tensile strength and modulus of the blend and blend nanocomposite fibers were improved due to the strong interface bonds between matrix and dispersed phase. The PS domains were less susceptible to deformation in the PP/PS/PP-g-MA/

organoclay during the process than in the PP/PS/PP-g-MA.

## Experimental

### Materials:

Commercial fiber grade isotactic PP, known as V30S, was obtained from Arak petrochemical Co., Iran. The PS was produced by shell chemical company with trade name of PB3150. The organically modified montmorillonite nanoclay (Cloisite15A) supplied by southern clay products Inc. were used as organoclay.

### Specimen preparation:

PS, PP-g-MA and organoclay were dried in vacuum oven for 24 h at 80°C. To obtain enough materials for mechanical property test, melt compounding was also conducted by using a co-rotating twin screw extruder (Z-Sky). The extrusion zone temperature ranged from 220 to 240°C and a screw speed of 120 rpm were used (the mixing time is less than 3min). The extrudates were palletized with hake pelletizer. The blend compositions are given in Table 2.

Before melt spinning, the polymer blends were dried in a vacuum oven for 24h at 80°C. Melt spinning process was performed on a single screw (L/D=26) Brabender melt extruder with a spinneret containing 20 orifices, each of 0.5 mm diameter. The extruder was set with five different temperature zones, 200, 210, 230, 240 and 250 °c, respectively, at the feed, metering and die and spinneret section. The screw was run at 60 rpm.

Table 2. Blending compositions

Sample	PP%	% PS	%PP-g-MA	% organoclay
1	80	15	5	---
2	70	25	5	---
3	60	35	5	---
4	75	25	---	---
5	79	15	5	1
6	77	15	5	3
7	75	15	5	5

### Characterization:

#### Scanning Electron Microscopy (SEM):

SEM images were taken to study the morphology of PP/PS blends with or without organoclay and compatibilizer. SEM micrographs were taken from cryogenically fractured surface of polyblend specimens after submersion in liquid nitrogen for 1h. The surface was then sputter coated with analyzer of gold palladium before viewing. The fractured surfaces of the samples were investigated in a SEM instrument, LE0440, operating at 20 kV.

### Thermal analysis:

Differential scanning calorimetry (DSC) spectra were recorded on Perkin-Elmer DSC Pyres-I. Thermal properties of samples were studied using Differential Scanning Calorimetry (DSC) at heating and cooling rates of 5°C/min. The samples were heated up to maximum temperature of 300°C, held there for 3 min and then allowed to cool to room temperature to analyze the non isothermal crystallization behavior of phases.

### X-ray diffraction analysis (XRD):

A Siemens x-ray diffraction unit operated at 30kV and 20mA, with Cu element and nickel filter was used to find the changes in crystallinity of samples.

### Mechanical testing:

Mechanical properties of the fibers were measured by an Instron tensile testing machine. The data were collected by a computer. The tensile modulus was measured as the slope of the stress-strain curve using a 10% min<sup>-1</sup> strain rate and a 500 g load cell. No slippage of filaments in the grips has been detected during the testing by this method. Ten filament were tested the average mechanical properties for each composition.

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