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Polypropylene/Polystyrene in situ nano reinforced blends fiber: Morphology and properties

ABSTRACT

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Polypropylene / polystyrene blends containing montmorillonite (MMT) were prepared using a twin screw extruder followed by fiber spinning. The melt intercalation of PP and PS alloys was carried out in the presence of a compatibilizer such as maleic anhydride-g-polypropylene (MPP). The crystallization morphology, thermal behaviors and mechanical properties of polypropylene/polystyrene (PP/PS) nanoclay blends nanocomposite fibers were investigated in the present work. The improved adhesion between the phases and fine morphology of the dispersed phase contributed to the significant improvement in the properties and thermal stability of the final nanocomposite materials. On the basis of this result, we describe a general understanding of how the morphology is related to the final properties of OMMT- incorporated PP/PS blends.

Keywords: *Polypropylene; Polystyrene; Blend; Organoclay; Nanocomposite; Morphology and properties.*

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 compatibilization is block or graft copolymers, which exhibit intermolecular attraction or chemical reactions with the blend components. Maleic anhydride-g-polypropylene (MAPP) is an effective precursor of the reactive compatibilizer for polypropylene (PP) and polar polymer blends [3]. The blends of polyolefins 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 process ability and low cost [4-8].

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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]. A new approach in the nanocomposites studies consists in nanocomposites based a blends of two or more polymeric materials [7]. In this direction, some studies related to nanocomposites of the blends have been reported, especially for polypropylene/polyamide-6/clay (PP/PA6/clay) blends [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 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 attribute this behavior to the ability of the clay of affecting both, the interfacial tension and the viscosity ratio, which are important factors in the determination of the size of dispersed phase during mixing [13,14]. The organically modified nanoclay may 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 modified MMT. Moreover, in the preceding studies, the added organoclay to the various blend was rather high, therefore an increase in viscosity could be the reason for the reduction in domain sites [15].

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

EXPERIMENTAL

Materials

Commercial fiber grade isotactic polypropylene (PP), known as V30 s, was obtained from Arak petrochemical co., Iran. Fiber grade polystyrene (PS) was produced by shell chemical company with trade name of PB3150 was received from Uniroyal chemical co. USA. The organically modified montmorillonite nanoclay (Cloisite15A) supplied by southern clay products Inc. were used as received for the melt blending.

Specimen preparation

Polystyrene (PS), maleic anhydride-g-polypropylene (MPP) and nanoclay were dried in vacuum oven for 24 hat 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 was used (the mixing time is less than 3min). The extrudates were palletized with hake pelletizer. The blend compositions are given in Table 1.

Table 1. Blending compositions.

Sample	PP%	% PS	%MPP	%Nanoclay
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

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 0.5mm 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 60rpm.

Characterization

- **Scanning Electron Microscopy (SEM)**

SEM images were taken to study the morphology of PP/PS blends with or without nanoclay 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, LEO440, operating at 20 kV.

- **Thermal analysis (DSC and TGA)**

Differential scanning calorimetry spectra were recorded on Perkin-Elmer DSC pyres-I differential scanning calorimeter calibrated the temperature and then crystallization behavior can be obtained. All DSC were performed under nitrogen atmosphere. In this experiment, about five milligrams of dried sample was first hold in 50°C for 5min, then heated quickly from 50 to 350 at 10°C/min and hold for 5min after reached 200°C in order to eliminate the influence of thermal history.

After that, the samples were cooled from 350 to 50°C (at- 10°C/min) and kept at 50°C for 1min. At last a heating scanning from 50 to 350°C (at 5°C_{min}) was carried out thermogravimetry

analysis was performed with a Perkin Elmer TGA7 thermal analysis system. The TGA scans were recorded at 10°C/min under a nitrogen atmosphere from 50 to 700°C.

- **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⁻¹ 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.

RESULTS AND DISCUSSION

Morphology of PS domain

A comparative study of the phase morphologies of the blends was performed by SEM (Figure 1). Polypropylene and polystyrene (PP and PS) is immiscible polymers, and the PS appeared as dispersed phase with irregular shape in the PP matrix. The specimens were analyzed at perpendicular direction to spinning flow (transverse/ direction) and parallel to spinning flow (longitudinal direction). Strain existed below the spinneret, which could deform the PS phase in fiber path.

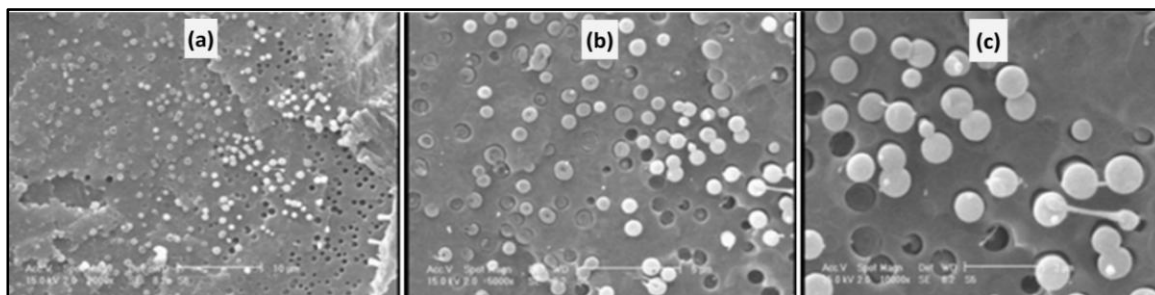


Fig. 1. SEM micrographs of the 1% nanoclay filled (79/15/5) PP/PS /MPP blend nanocomposite fiber at four different magnifications. (a) Low zoom (b) Moderate zoom (c) High zoom.

According to Figure 1 (a, b and c) the white domains represent the position of the PS dispersed phase in the PP matrix. Both the interparticle distance and the size of the dispersed PS phase are found to decrease by adding nanoclay. However, due to the complexity of flow in and extruder, it is difficult to assert that the nature of the flow is responsible of the morphology obtained. Regarding the coalescence mechanism, nanoclay layers prevent the coalescence rate and consequently promote droplet size reduction as the balance between break up and coalescence is shifted to the break up mechanism. This could be explained by the fact that the polymer pairs of PP and PS are thermodynamically immiscible. To play this role, nanoclay should be at least partially exfoliated and should have some interactions with both phases.

Thermal Analysis

The results of DSC analysis of samples are summarized in Table 2, polyblend fibers and polyblend nanocomposite fibers exhibited two distinct melting peaks, the lower obviously corresponding to the melting point of PP whereas the higher corresponding to the melting of PS. Since the neat PP and PS fibers showed only one melting peak each the two polymers could in general be considered as immiscible.

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 a result of the formation of block copolymer between PP-g-MAH and PS. One of the results noted is that the crystallinity of PS in the polyblend fibers is higher than the value of neat fibers. This most likely indicates that PP molecules acted as nucleating agents for PS in the polyblend fiber.

A similar increase in crystallinity did not take place for PP. such nucleating effect was other reported for organoclays and compatibilizers. The crystallization of the PS phase increased slightly with addition of organoclay, and the increase was a bit more pronounced for MAH-g-PP compatibilized PP/PS polyblend nanocomposite fibers. The remaining ashes were attributed to the high thermal stability of montmorillonite. This result was in agreement with the data sheets of the organoclay supplier. It is generally accepted that the incorporation of layered silicate platelets in to polymeric materials can improve their thermal stabilities.

In the case of clay-containing polymer nanocomposites, the increase in thermal stability can attributed to an ablative reassembling of the silicate layer which may occur on the surface of the nanocomposites creating a physical protective barrier on the material.

However, the improvement in thermal stability of polymer/ nanoclay nanocomposites is directly related to the degree of dispersion of silicate layers in the polymer matrix. In the case of polymer blend nanocomposites, the thermal stability is also controlled by the final morphology of dispersed phase.

Table 2. DSC thermal properties and percent crystallinity for fibers.

Samples	T_m of PP (°C)	T_m of PS (°C)	Crystallinity PP (%)	Crystallinity PS (%)	Total Crystallinity (%)
PP	166.5	-	37.03	-	37.03
PTT	-	231.3	-	23	23
2	167.7	229.2	42.2	33.92	40.1
3	167	229.3	39.62	19.7	38.2
4	167.9	229.4	50	25.58	41.5
5	166.7	228.5	47	23	40.6
7	167.3	228.8	47.15	19.9	38.25

Wide angle x-ray diffraction analysis

The X-ray diffraction patterns of polyblend and polyblend nanocomposite fibers are shown in Figure 2. According to this Figures 2(a, b, c, d, e, f, g) 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° of 14.2, 16.8 and 18.6 corresponding, respectively, to the 110, 040, and 130 planes of PP and 2° of 15° 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.

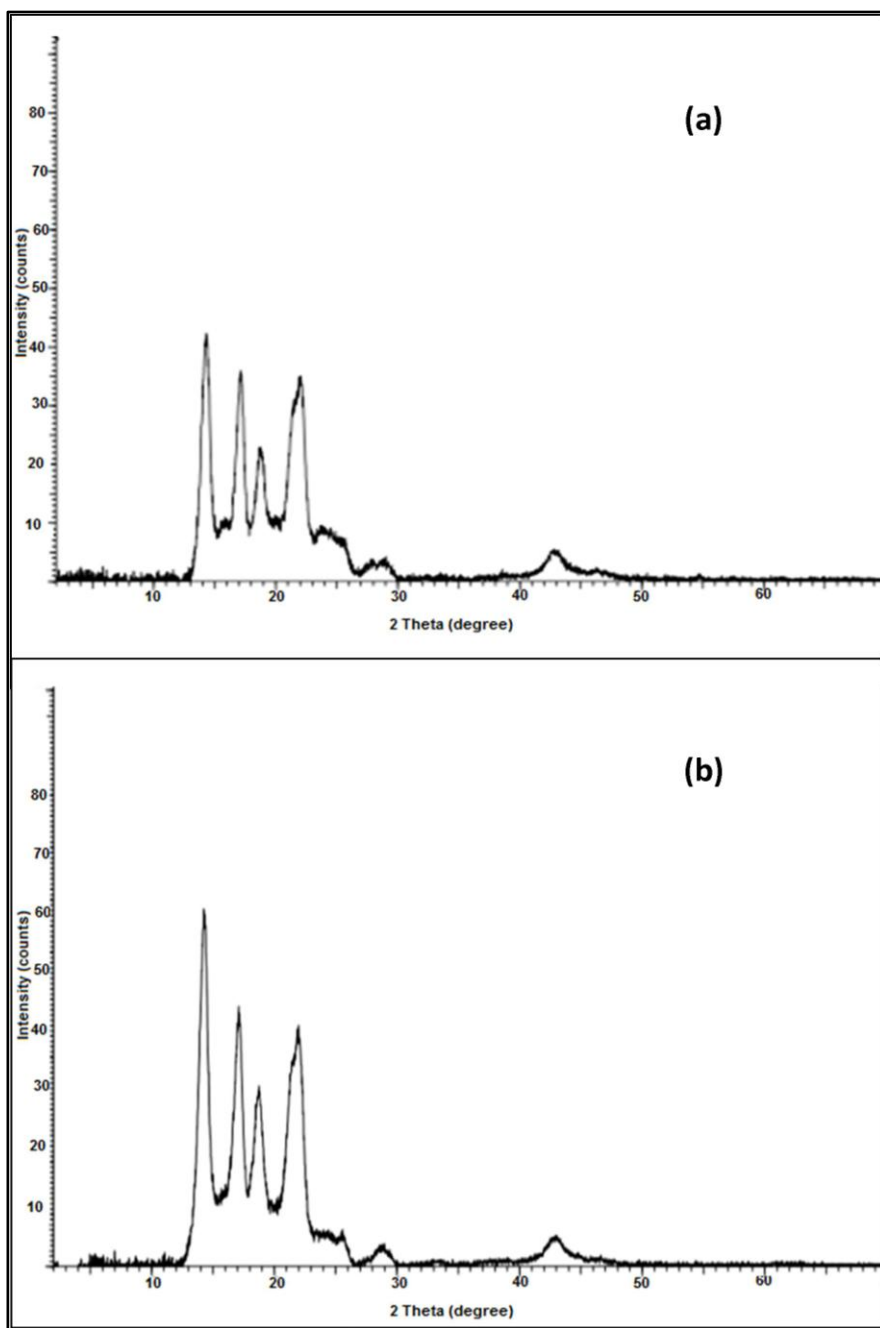


Fig. 2 (a & b). Wide angle x-ray diffraction spectra of different samples sample 1 & 2.

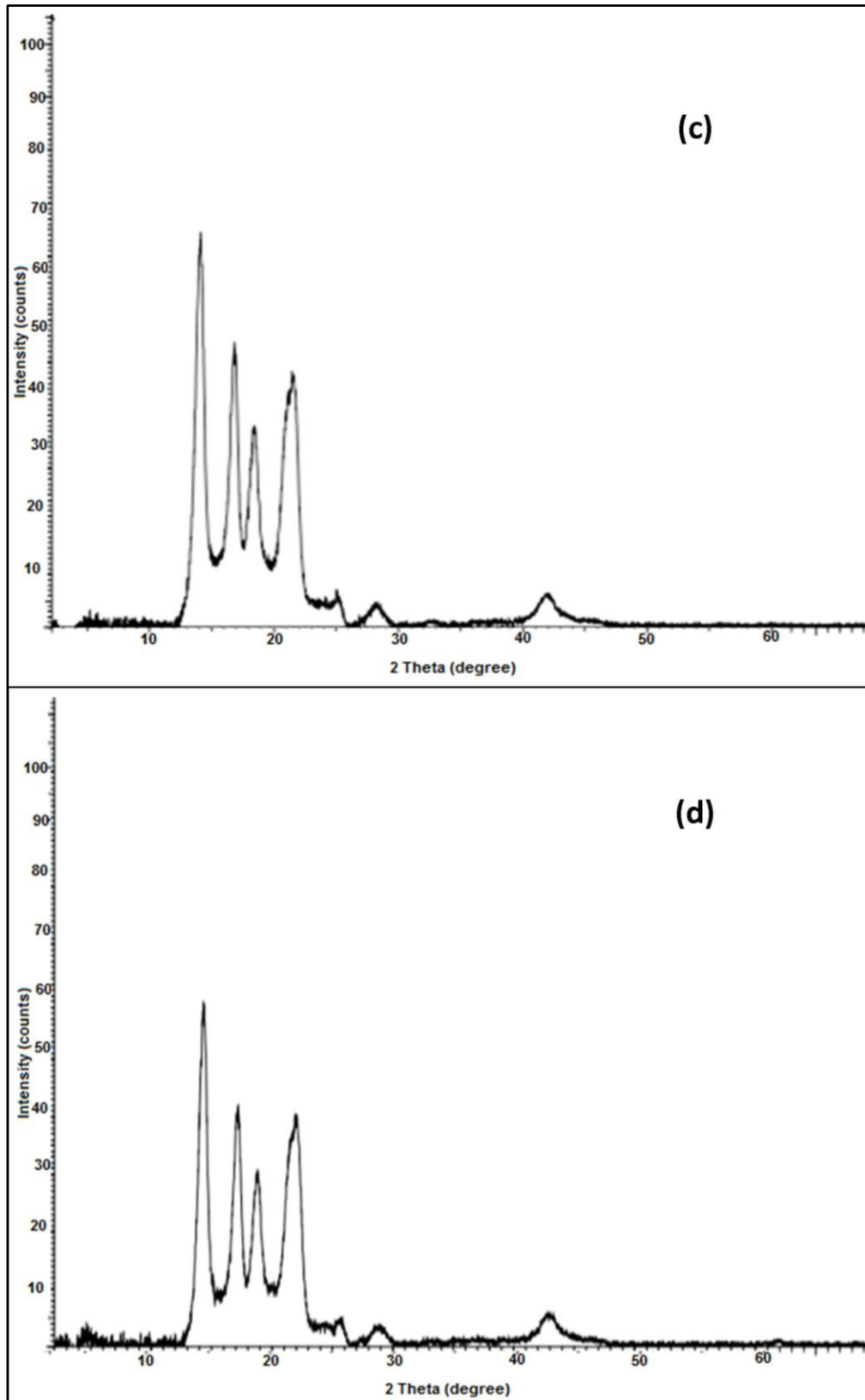


Fig. 2 (c & d). Wide angle x-ray diffraction spectra of different samples sample 2 & 3.

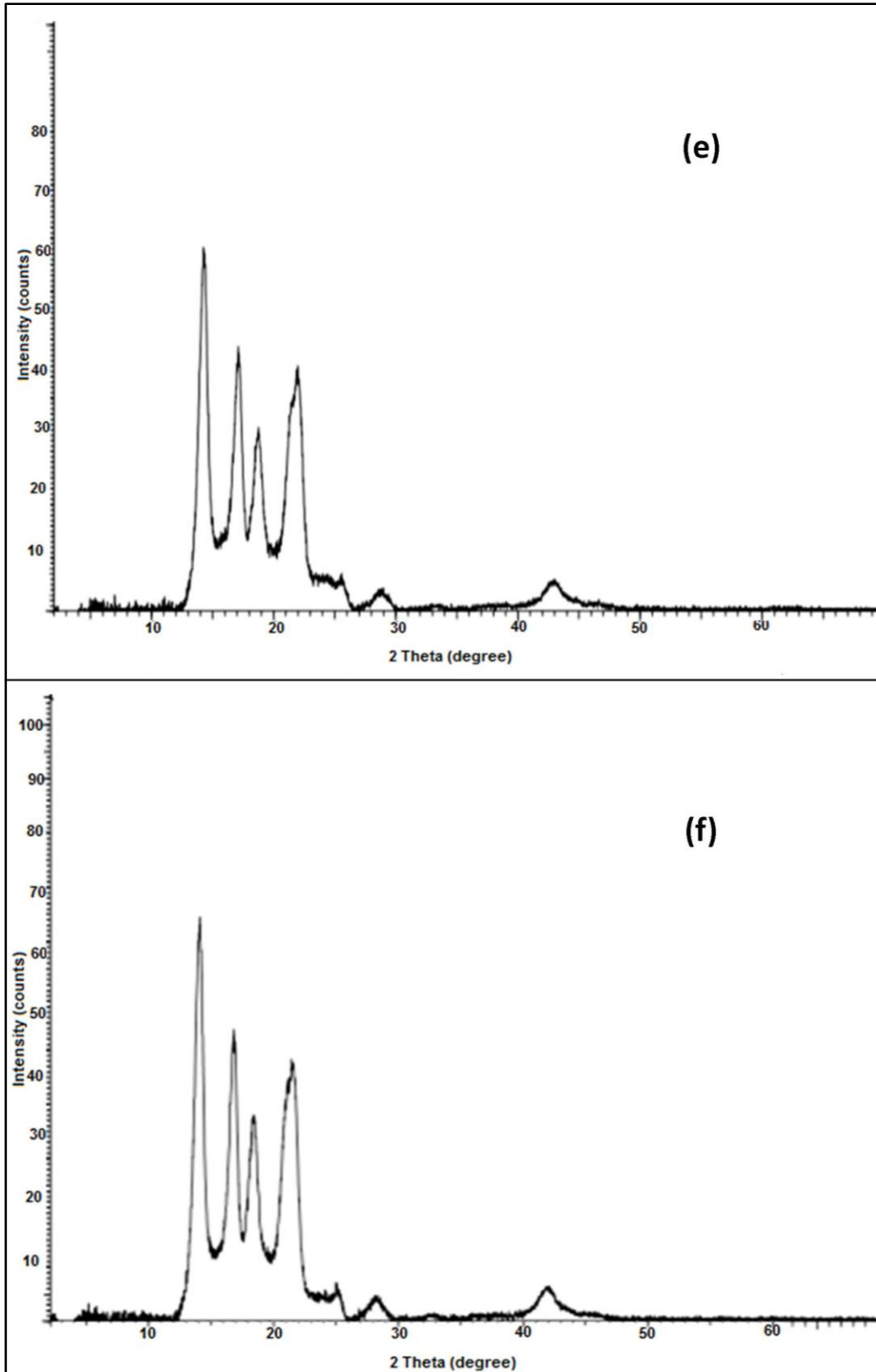


Fig. 2 (e & f). Wide angle x-ray diffraction spectra of different samples sample 5 & 6.

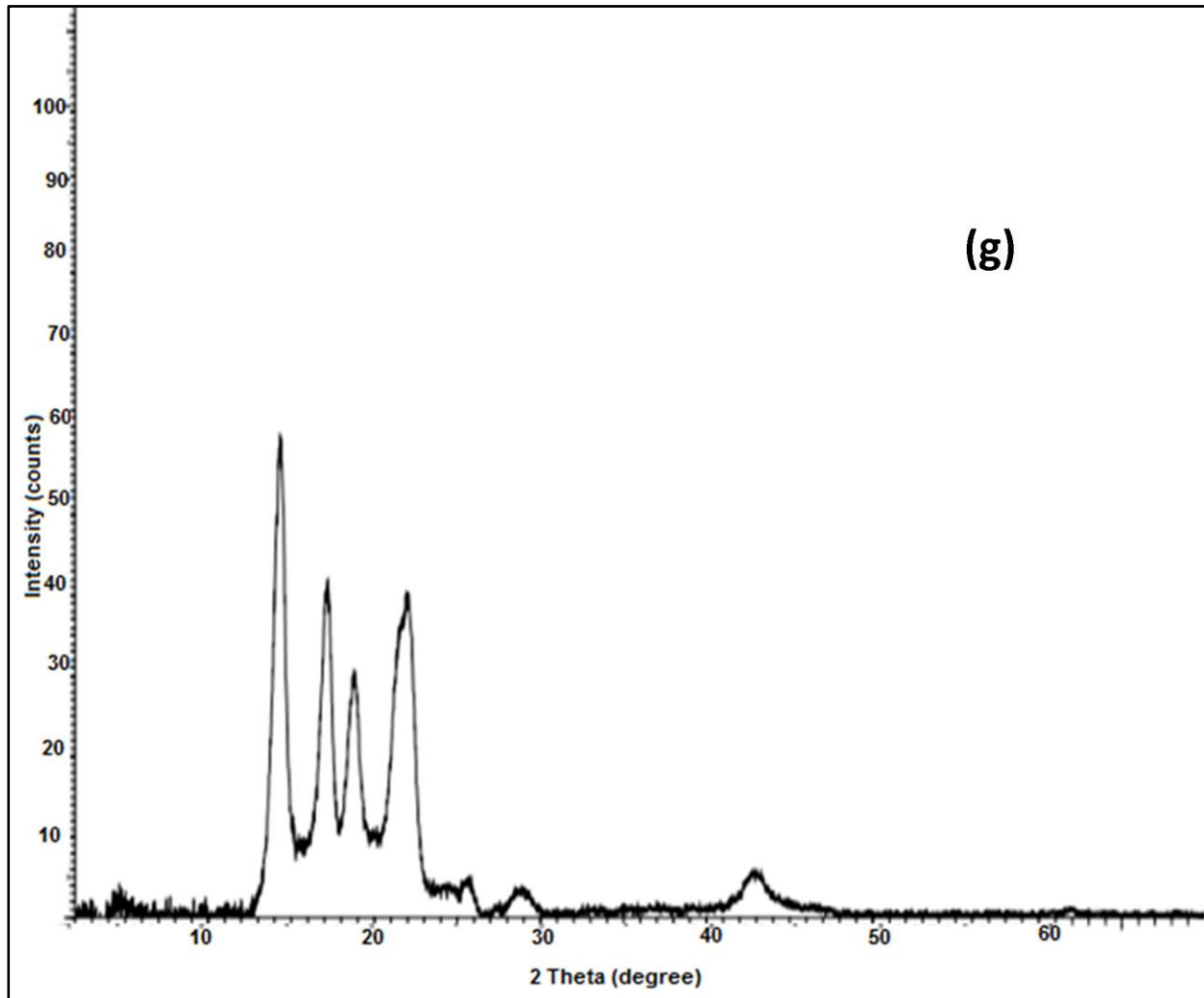


Fig. 2(g). Sample 7
 Fig. 2. Wide angle x-ray diffraction spectra of different samples (Samples 1- 7).

Mechanical properties

Tensile strength (Figure 3a), modulus (Figure 3b) and elongation at break (Figure 3c) of different PP/PS blend fibers with and without nanoclay and compatibilizer are listed in this figure (Figure 3). The test results showed that the addition of PP-g-MA indeed improve the compatibilization of the PP/PS blends were better than that of pure PP fibers because of the formation of in situ micro PS fibers. The PP/PS/MPP/nanoclay blend nanocomposite fibers had better mechanical properties than the blend. Fibers without nanoclay the tensile mechanical properties of the hybrid fibers were found to be increased with increasing organoclay content, where increases in content

from 3 to 5 wt. %. It was 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 nanoclay 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.

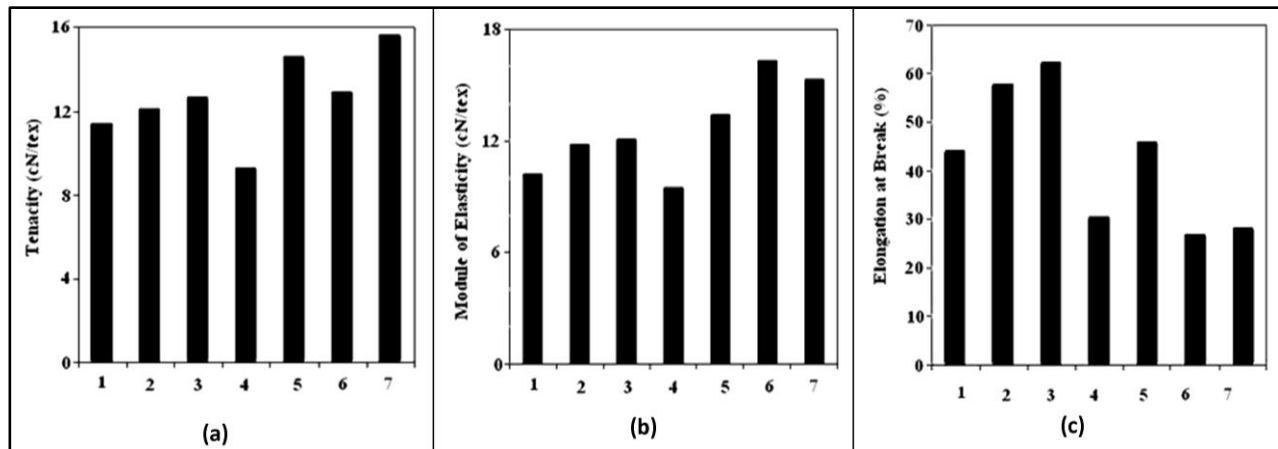


Fig. 3. Tensile properties of hybrid fibers.
(a) Tenacity (b) Modulus of elasticity (c) Elongation at break.

CONCLUSIONS

In this study, the effect of added of organically modified nanoclay and maleic anhydride-g-polypropylene PP-g-MA and different blend ratio on the morphology and properties of immiscible polypropylene polystyrene blend fibers were investigated. The compatibility of PP/PS blends can be dramatically improved with the addition of nanoclay and PP-g-MA, which have excellent effect to reduce interfacial tension. Selective localization of nanoclay at the interface of immiscible polypropylene/polystyrene (PP/PS) polymer blend can be achieved by introducing a copolymer that preferentially localizes at the blend interface which has the highest affinity for nanoclay.

PS disperse phase likes nanoclay 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 disperse phase. The PS domains were less susceptible to deformation in the PP/PS /MPP/nanoclay during the porous than in the PP/PS/MPP. The optimum result was observed when simultaneously PP-g-MA and nanoclay were use. The crystallization, melting behavior and polymorphic composition of PP in non-compatible and compatibilized PP/PS blends were related to PS content, compatibilizer and nanoclay content.

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