PET/PP Blending by Using PP-*g*-MA Synthesized by Solid Phase

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ABSTRACT: In attempts to improve the compatibility of polypropylene (PP) with polyethylene terephthalate (PET), a maleic anhydride grafted PP (PP-*g*-MA) was evaluated as a compatibilizer in a blend of 30/70 wt % PP/PET. PP-*g*-MA was produced from isotactic homopolymer PP utilizing the technique of solid phase graft copolymerization. Qualitative confirmations of the grafting were made by Fourier transform infrared spectroscopy (FTIR). Three different weight percent of compatibilizer, PP-*g*-MA, i.e., 5, 10, and 15 wt % have been used in PP/PET blends. The compatibilizing efficiency for PP/PET blend was examined using differential scanning calorimetry (DSC), optical microscopy (OM), scanning electron microscopy (SEM) of crycrofractured surfaces, and energy dispersive X-ray spectrum (EDAX). The results show that the grafted PP promotes a fine dispersed phase morphology, improves processability, and modifies the crystallization behavior of the polyester component. These effects are attributed to enhance phase interaction resulting in reduced interfacial tension. Also, the results show that the compatibilizing effects of the three amounts of grafted PP in blend are different and dependent on the amount used. Adding 10 wt % of compatibilizer into blend produced the finest dispersed morphology. Elemental analysis results show that PP is matrix. DSC determination revealed that the melting temperature (T_m) of the PET component declined to some extent by comparison with neat PET. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104, 3986–3993, 2007

Key words: compatibilization; grafted PP; solid phase; PP/PET blending

INTRODUCTION

Immiscible polymer blends are often preferred over the miscible types since they may combine some of the important characteristics of each blend component. Minimizing interfacial tension and improving adhesion between two phases usually attains satisfactory performance in immiscible blends.[1,2]

Compatibility of immiscible blends may be improved by adding a third compatibilizing component (e.g., block or graft copolymers) or by adding suitable functionalized polymers capable of enhancing specific interactions and chemical reactions in reactive systems. A copolymer may be formed *in situ* during mixing, acting in similar manner as the above compatibilizer added separately.[3]

Polypropylene-maleic anhydride copolymers were first synthesized by grafting maleic anhydride to polypropylene in the early 1960s.[4] The synthesis was performed in the liquid phase using benzene or toluene as the reaction medium. Several free radical initiators were used to initiate the reaction. The reactions were performed in solution at the boiling point of the solvent. The duration of the reaction varied from 1 h to over 20 h the comonomer content in the graft copolymer varied from 0.3 to 40%. The resultant polymer was dark brown in color. In certain cases, salts of the above polymers were prepared by further reacting with calcium or zinc salts.

Graft copolymers were also produced by extrusion processes that provide very low levels of graft (∼ 0.4%) using twin screw extruders. The graft level was primarily determined by the residence time in the extruder. The reaction was performed at high temperatures (>250°C). High shear developed in the twin screw extruder that ensured uniform mixing in the extruder. The free radical initiator used had an extremely low halftime at the processing temperatures, which partially accounted for the low graft levels.[5]

Graft copolymerization of polypropylene (PP) and maleic anhydride was also performed in single screw extruders. The primary objective of these studies was to investigate the feasibility of producing graft copolymers in an extruder and to improve the surface properties, specially, the adhesion of the copolymer to other substrates.

Currently, the copolymer of PP and maleic anhydride is being used as an adhesive layer in laminates. These adhesives have been used to bond two nonadhering polymers. The adhesive is either coated on one

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substrate and then melt bonded onto the other or a thin layer of adhesive film is coextruded and laminated to form a permanent bond. The peel strength of the laminate increased with the amount of reactive component in the copolymer.[6]

As pointed out by Lee et al.,[7] solid phase grafting has several advantages over other processes such as low amount of solvent was used; no solvent recovery; low temperature, low pressure, and low residence time; and low shear mixer was applied.

Polyethylene terephthalate (PET) and PP are not compatible and their blending will produce large phases with weak interfacial bonding and poor mechanical properties. Although these two polymers are major polymers, but literature studies show few works on this subject, and besides there is no commercial polyolefin/polyester blend on the market.[8,9] The work on PET/PP blends stemmed from our interests in recycling postconsumer plastics. Potential markets for recycled plastics are numerous, e.g., geo-textiles, park benches, garbage cans, and highway post.

The suitability of these polymers for blending can be assessed by their individual characteristics. The melting point T_m and glass transition temperatures T_g of PET (250°C and 80°C, respectively) are higher than PP (165°C and 7–10°C, respectively).

Consequently, PET could be expected to be capable of reinforcing PP at higher temperatures. PET is generally stiffer than PP because of the presence of fewer methylene groups between the stiffening groups such as carbonyl and phenylene groups.

Since the permeability of PET to gases is much lower than PP and permeability to water is higher than PP,[10] a blend could be expected to combine the barrier properties of both components. The polymers are also complementary in their resistance to solvent and chemical attack.

The structural differences which are responsible for the differences in resistance to solvent and chemical attack also result in different types of chemical modification. These various complementary features together with the limited extent to which studies on PET/PP blends have been reported in the literature and the economic importance of both types of polymer, it is suggested that these blends might make a suitable topic for investigation.

According to theoretical model of polymer blending, the ability to control blend morphology and properties depends basically on the mixing process, the rheology of components, and the interfacial properties.[11–13] Compatibilization can be achieved by melt blending of two polymers containing functional groups that react with each other. In such case, a graft copolymer is formed *in situ* during melt blending. Recently, much attention has been directed towards functionalized PP (e.g., PP-MA) with polyester.[14]

In a study that has been carried out recently by Chiu and Hsiao,[15] the compatibilization of PET/PP blends were investigated by using a maleic anhydride grafted polyethylene-octene elastomer (POE-*g*-MA) as the compatibilizing agent. The olefinic segment of POE is compatible with PP, whereas the maleic anhydride is affined with PET carbonyl groups. The compatibilization of PET and PP has also been carried out by using a modified polypropylene grafted with an unsaturated carboxylic acid or its anhydride.[16]

The aim of this study is preparation of PP/PET blends using maleic anhydride grafted PP (PP-*g*-MA) compatibilizer, which produced from solid phase grafting process.

EXPERIMENTAL

Materials

Polypropylene (grade: V30S, MFI = 16 g/10 min) and Poly(ethylene terephthalate) (PET, melt temperature = 265°C, density = 1.41 g/cm^3) used in this work were produced by the Arak Petrochemical Co. (Arak, Iran) and Yazd Polyester Co. (Yazd, Iran), respectively. The polypropylene (PP) grafted MA was prepared by solid phase in our laboratory. Maleic anhydride (MA) with purity 99% was purchased from Merck (Germany). Benzoyl peroxide (BPO, 99% pure) was used as an initiator. It was obtained in a powder form by Merck (Germany). Xylene, a mixture of meta- and para- derivatives was used as interfacial agent and produced from Isfahan Petrochemical Co. (Isfahan, Iran). PP antioxidant, Irganox 1010, was purchased from the Ciba-Geigy Chemical Materials Company (Basel, Switzerland).

Processing

Solid phase grafting of PP with MA

The functionalization of PP was carried out by solid phase graft copolymerization using four-neck flask equipped with an agitator, operating at 100 rpm. PP powders (15 g) were weighed and added into the reactor. Then 1 g of xylene was added and the agitator was turned on and was allowed to reach reaction temperature (130°C). During this period nitrogen was purged into the reactor. The additives were added in two stages. After 10 min, 0.5 g of the comonomer (MA) and 0.5 g of the initiator (BPO) were divided to two equal parts and each part was added into the reactor at 16 min intervals. The reaction was terminated after 32 min when the last batch of MA and BPO were added. Total time of the reaction was 58 min. The reaction product was extracted with acetone to remove the unreacted monomers and oligomers. The semipurified product was dried at 80°C for 1 h in a vacuum oven.

TABLE I
Blends Composition Used in This Study

Trial no.	PET/PP-*g*-MA/PP (w/w %)
1	70/0/30
2	66.5/5/28.5
3	63/10/27
4	59.5/15/25.5

Blending of PP with PET

Four blends containing different weight percent of PET, PP, and compatibilizer, (Table I), were compounded in an internal mixer running at 40 rpm. The volume of the mixing chamber (corrected for rotors) was 55 mL and the fill factor was taken as 0.7 so that the net capacity for mixing materials was 38.5 mL. The temperature setting of the brabender was 265°C. The amount of antioxidant which used in each component was 0.1 wt %.

Characterization

Infrared spectroscopy

PP grafted MA samples were pressed into thin films by compression molding in a hot press. A Bauman MB100 Fourier transform infrared spectroscopy (FTIR) spectrometer was used. Prior to FTIR spectroscopy, a sheet of maleic anhydride grafted PP (PP-*g*-MA) was prepared by press molding of 4 g of PP-*g*-MA of sample. Then FTIR spectrum was taken from molten film of PP-*g*-MA.

Optical microscopy

Optical micrographs of PP/PET blends were obtained with a Motic B3 model microscope equipped with CCD camera. The specimens were prepared by cutting the molten cross section of blends using a rotating microtome.

Scanning electron microscopy

Morphological observation of PP/PET blends were carried out by scanning electron microscopy (SEM). Cryofractured surfaces of the blends were imaged using a Philips lx-30 scanning electron microscope.

Thermal analysis

Differential scanning calorimetry (DSC) measurements were carried out using the DuPont DSC 910. The running conditions were: heating rate: 3°C/min and N_2 flow rate: 60 mL/min. All samples were heated from 25°C to 300°C.

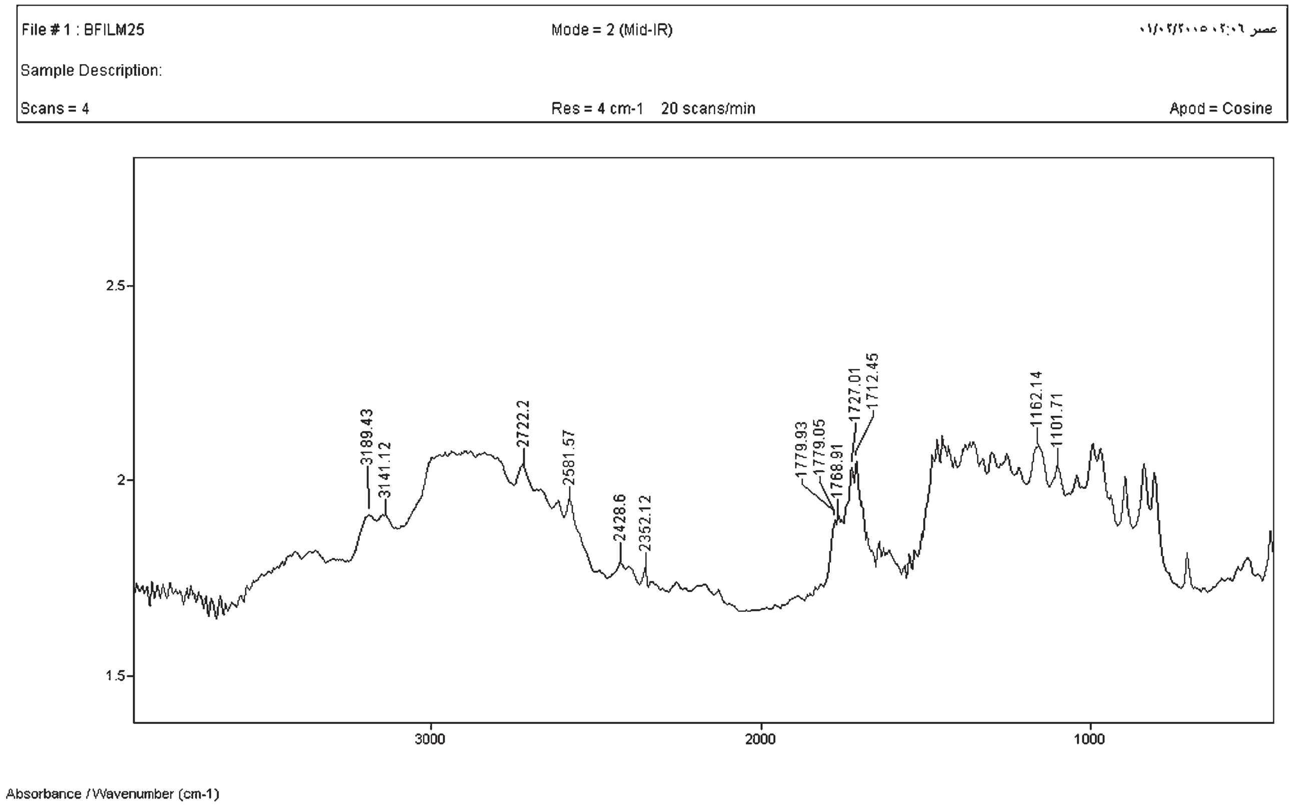


Figure 1 FTIR spectrum of compatibilizer (PP-*g*-MA).

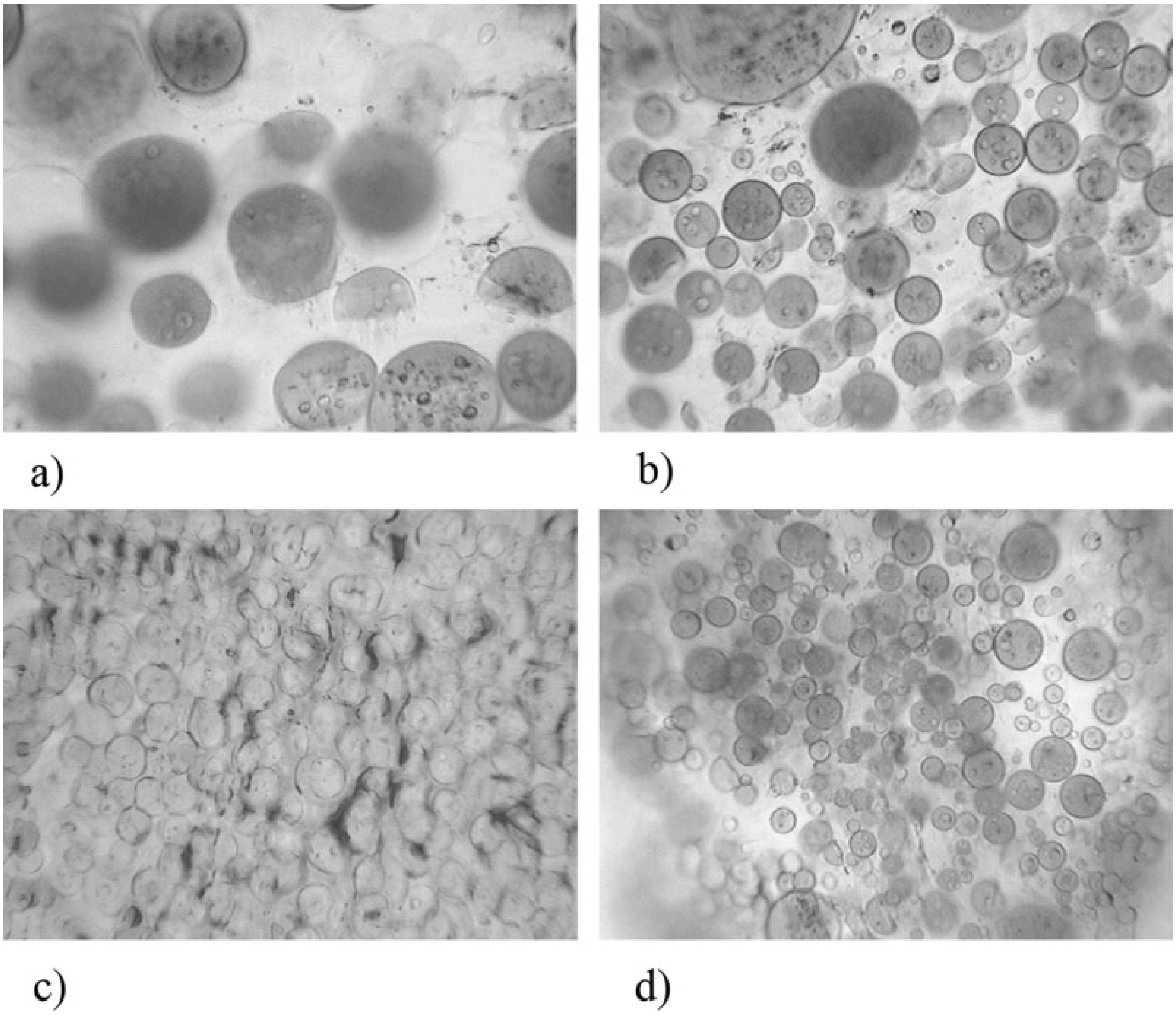


Figure 2 OM micrographs of PP/PET blends, (a) without compatibilizer; (b, c, d) with 5, 10, 15 wt % compatibilizer, respectively.

RESULTS AND DISCUSSION

FTIR spectroscopy analysis of the compatibilizer

Fourier transform infrared spectroscopy (FTIR) analysis was performed on all the samples. A sample FTIR spectrum of trial 25 is shown in Figure 1. It can be seen from Figure 1 that the grafted PP sample shows absorbance bands at 1710 and 1780 cm^{-1} assigned to the presence of maleic acid and maleic anhydride oligomer,[17,18] respectively, indicating the grafting of the MA onto the PP main chains. It is clear that the maleic anhydride peaks as identified in the infrared spectrum are from the copolymer and not from the free maleic anhydride. It was ensured that the free unreacted maleic anhydride was removed by extraction with water.

Morphology

Optical and SEM microscopy

OM micrographs of PP/PET blends are shown in Figure 2. Unmodified PP is incompatible and poorly dispersed in PET. This is in line with the mechanism of the reactive compatibilization. Increase of PP-*g*-MA leads to poor dispersion of PET domains while at high compatibilization content crystallinity development is limited.

The SEM micrographs of PP/PET blends compatibilized with the different amounts of compatibilizer are presented in Figure 3. It is seen that these amounts of compatibilizer result in entirely different morphologies. Without compatibilizer, the blend shows a dispersed PET phase with irregular shapes and sizes, and even a large fraction of the domains is fiber-like.

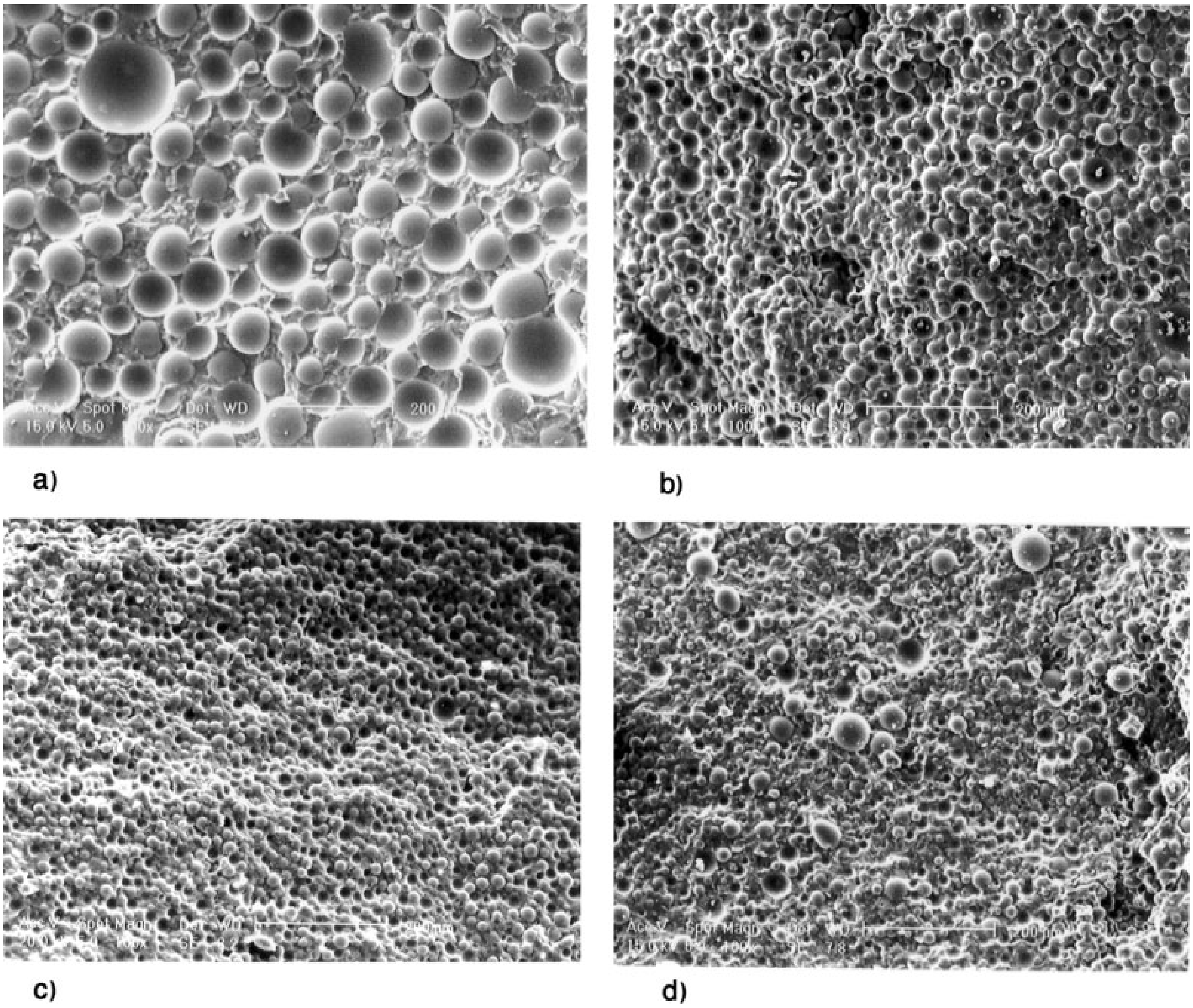


Figure 3 SEM micrographs of PP/PET blends, (a) without compatibilizer; (b, c, d) with 5, 10, 15 wt % compatibilizer, respectively.

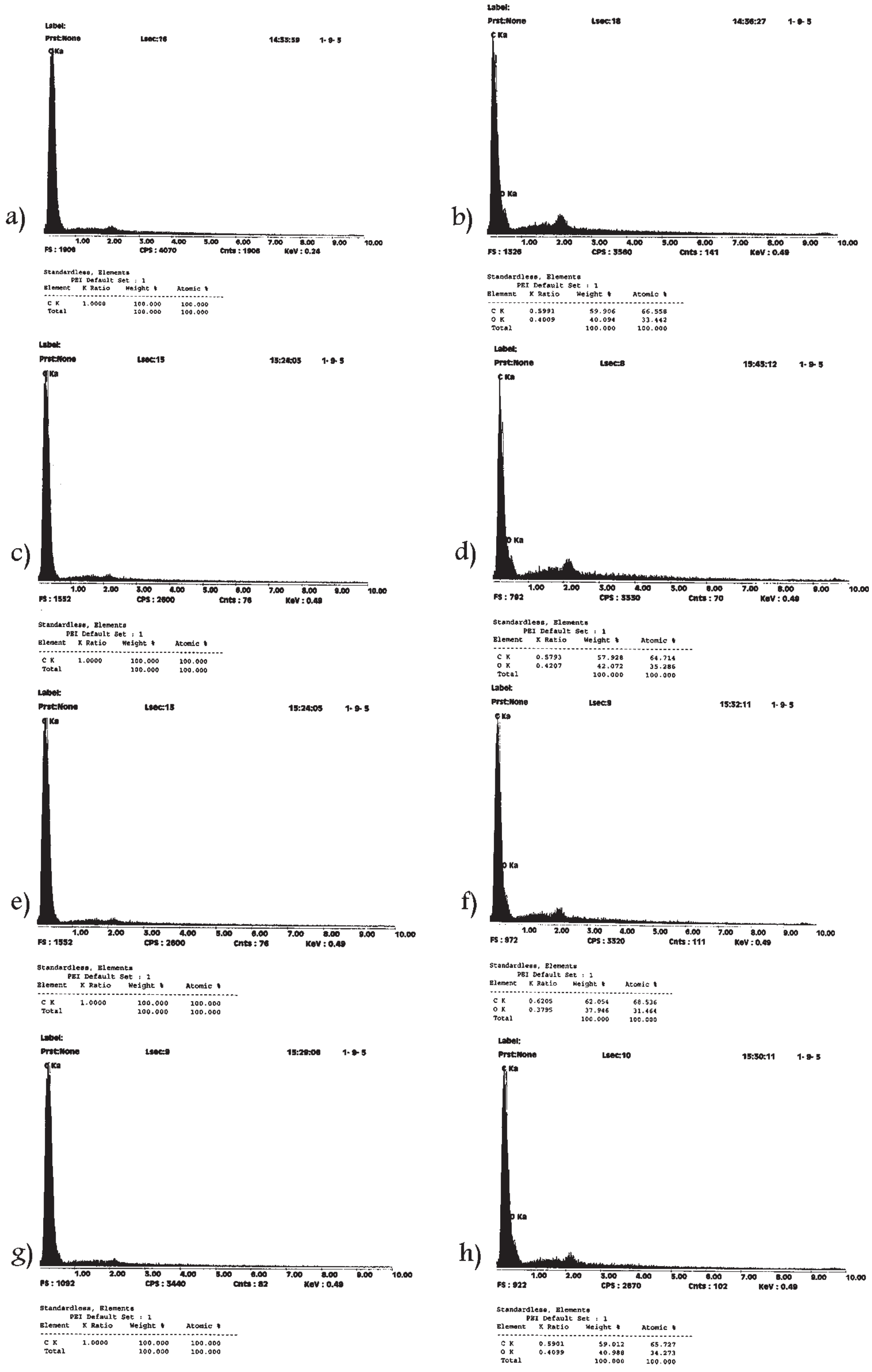
The addition of compatibilizer produced regular shaped and relative uniformly sized PET domains. The PET domain sizes strongly are dependent upon the amount of compatibilizer used.

It is widely accepted that a compatibilizer has two main roles in the control of morphology of a blend, that is, prevention of coalescence and reduction of interfacial tension.[19–21] The uniformity of shape and size of the PET domains caused by addition of compatibilizer is believed to be the result of reduction of coalescence because of the steric stabilization role of compatibilizer. In contrast, the change of PET domain sizes with the various amounts of compatibilizer is considered to be caused by the different events of decrease in interfacial tension.

Elemental analysis

To investigate chemical basis of dispersed and matrix phases, energy dispersive X-ray spectrum (EDAX) was used. Figure 4 shows elemental analysis (EDAX) diagrams. Right diagrams indicate the dispersed phase and left diagrams are related to the matrix phase. In EDAX diagrams of all the blends, it is seen that carbon and oxygen peaks present in dispersed phase, while only the carbon peak is observed in matrix phase. It indicates that in all the blends, polyester is dispersed phase and polypropylene is matrix phase. That is due to higher interfacial tension of PET rather than PP. On the other hand, PP has lower viscosity than PET in process conditions; therefore, this will result in increased PP movement in blend and consequently increased fluidity and continuity of PP to have the role of matrix phase.

According to Figure 5, the viscosity of PP is higher than PET in normal state. But with increasing shear rate to values higher than 100 s^{-1}, PET diagram crosses the PP ones and results in higher viscosity of PET relative to PP.[22]



a)

```
Standardless, Elements
       PEI Default Set : 1
Element   K Ratio    Weight %    Atomic %
------------------------------------------
 C K       1.0000     100.000    100.000
 Total                100.000    100.000
```

b)

```
Standardless, Elements
       PEI Default Set : 1
Element   K Ratio    Weight %    Atomic %
------------------------------------------
 C K       0.5991      59.906     66.558
 O K       0.4009      40.094     33.442
 Total                100.000    100.000
```

c)

```
Standardless, Elements
       PEI Default Set : 1
Element   K Ratio    Weight %    Atomic %
------------------------------------------
 C K       1.0000     100.000    100.000
 Total                100.000    100.000
```

d)

```
Standardless, Elements
       PEI Default Set : 1
Element   K Ratio    Weight %    Atomic %
------------------------------------------
 C K       0.5793      57.928     64.714
 O K       0.4207      42.072     35.286
 Total                100.000    100.000
```

e)

```
Standardless, Elements
       PEI Default Set : 1
Element   K Ratio    Weight %    Atomic %
------------------------------------------
 C K       1.0000     100.000    100.000
 Total                100.000    100.000
```

f)

```
Standardless, Elements
       PEI Default Set : 1
Element   K Ratio    Weight %    Atomic %
------------------------------------------
 C K       0.6205      62.054     68.536
 O K       0.3795      37.946     31.464
 Total                100.000    100.000
```

g)

```
Standardless, Elements
       PEI Default Set : 1
Element   K Ratio    Weight %    Atomic %
------------------------------------------
 C K       1.0000     100.000    100.000
 Total                100.000    100.000
```

h)

```
Standardless, Elements
       PEI Default Set : 1
Element   K Ratio    Weight %    Atomic %
------------------------------------------
 C K       0.5901      59.012     65.727
 O K       0.4099      40.988     34.273
 Total                100.000    100.000
```

Figure 4 Elemental analysis (EDAX) diagrams of PP/PET blends, (a–b) without compatibilizer; (c–d, e–f, g–h) with 5, 10, 15 wt % compatibilizer, respectively.

Thermal analysis

In addition to the observed morphology changes, the effects of compatibilization on polymer blends can also be investigated by determination of their thermal properties. The DSC results for neat PP and PET for the uncompatibilized and for the compatibilized blends are shown in Figure 6. It is seen that the melting peaks of PP in the blends are actually the same as

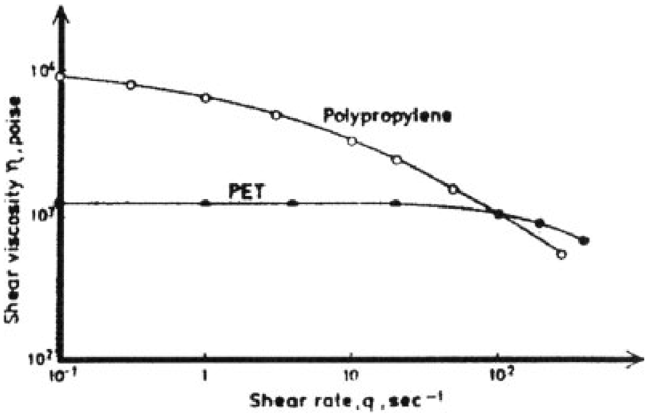


Figure 5 Viscosity dependence of PET and PP to shear rate.

that in pure state. All the melting temperatures are about 165°C, as listed in Table II. These results are easy to understand if it is remembered that PP is the major phase in the blends. However, the melting enthalpies (ΔH_m) of PP components are slightly lower than that of neat PP (Table II). It is interesting that the changing trend in ΔH_m for PP component basically correlates to the morphology changes of the blends: the finer the dispersed phase, the lower is the ΔH_m value. These results are related to the increase of interfaces in the blends, which leads to a decrease of weight fraction of the bulk PP.[23,24] In contrast, for the PET component the melting and crystalline peaks move somewhat towards low temperatures, specially the crystallization temperatures.

The crystallization behavior of the minor component in these blends has been suggested to be due to migration of nuclei across the interface and to nucleating agent-like behavior of the already crystallized minor component, or to an altered chain mobility in the interface.[3] According to the above-mentioned arguments, the PP provides nucleation sites for crystal formation. The thermal behavior of PET with functionalized PP blends showed that the T_m of PET in the PET/PP-*g*-MA blends are decreased by increasing the amount of functionalized PP, while the T_m of functionalized PP increased by decreasing the amount of PET in the blends.

CONCLUSION

It is clear that graft copolymers of polypropylene and maleic anhydride can be manufactured utilizing this energy-efficient, low-cost, low-temperature, low-pressure process. This process eliminated expensive solvent recovery and purification. This process also enables to prepare high comonomer levels unlike other processes. A high level of maleic anhydride can be grafted to polypropylene by this solid phase graft copolymerization process. This process utilized low amounts of solvent and can be performed at low temperatures (100–120°C) and at atmospheric pressure. This free radical process requires inexpensive reactor setup. By utilizing this technology the manufacture of copolymers of PP-*g*-MA is made easy and less expensive.

The compatibilizing effects of the three MA grafted PPs for PP/PET blends are dependent upon their amounts. Optical microscopy (OM) and SEM observed morphologies show that adding 10 wt % of

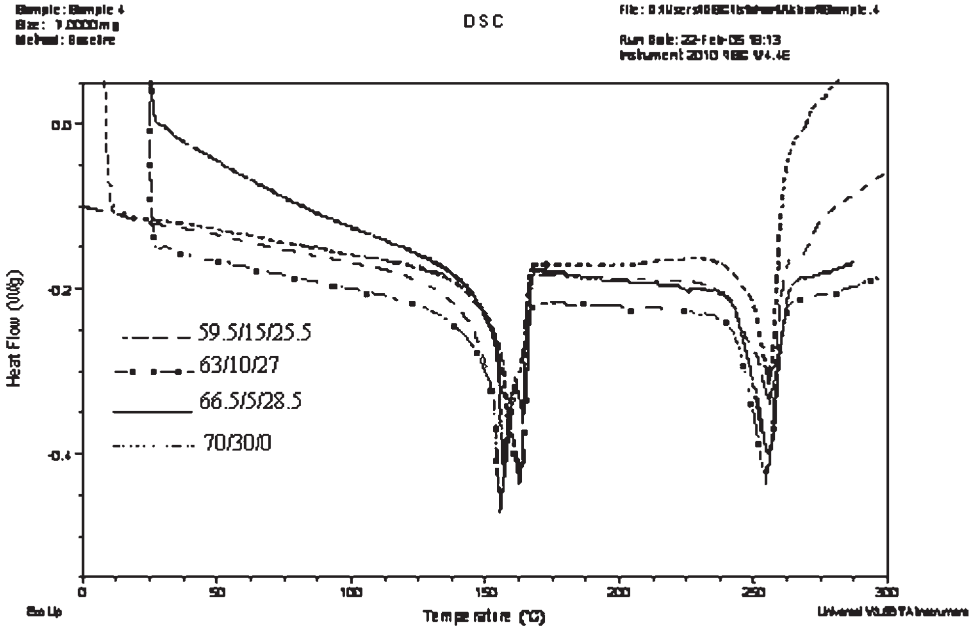


Figure 6 DSC results for neat PP and PET, for the uncompatibilized and for the compatibilized blends.

TABLE II
Results Obtained from DSC Measurements

Trial no.	Melting point of PET	Melting point of PP	Melting point of PP-*g*-MA	ΔH_{PET}	ΔH_{PP}	Crystallinity of PET	Crystallinity of PP
1	256.36	159.11	–	–	31.38	–	15%
2	255.67	157.11	163.78	29.46	35.12	23.5%	17%
3	255.20	155.82	163.29	29.34	39.09	23.3%	18.7%
4	256.07	155.76	162.97	26.65	46.15	21.2%	22%

PP-*g*-MA into these blends is the most effective one among them as it produced the finest PET domain size. The results of elemental analysis (EDAX) for PP/PET blends with different amounts of PP-*g*-MA compatibilizer indicate that in all the cases PET is dispersed phase and PP is the matrix phase. DSC measurements revealed that the change of T_m with compatibilization, which is related to the domain sizes, is also an indication of improvement of interfacial interaction.

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