Novel Multimonomer-Grafted Polypropylene Preparation and Application in Polypropylene/ Poly(vinyl chloride) Blends

Lianlong Hou,[1,2] Min Zhao,[3] Hongzhi Liu,[1,2] Guisheng Yang[1,4]

[1]*Key Laboratory of Engineering Plastics, Joint Laboratory of Polymer Science and Materials, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, People's Republic of China*
[2]*Graduate School, Chinese Academy of Sciences, Beijing 100039, People's Republic of China*
[3]*Department of Fire Technology, People's Armed Police Academy, Hebei 065000, People's Republic of China*
[4]*Shanghai Genius Advanced Materials Company, Limited, Shanghai 201109, People's Republic of China*

ABSTRACT: A novel grafted polymer was prepared in one step through free-radical melt grafting in a single-screw extruder. It was shown that the addition of styrene (St) to the melt-grafting system as a comonomer could significantly enhance the grafting degree of methyl methacrylate (MMA) onto polypropylene (PP) and reduce the degradation of the PP matrix by means of Fourier transform infrared and melt flow rate testing, respectively. Then, the potential of using multimonomer-grafted PP, which was designated PP-*g*-(St-*co*-MMA), as the compatibilizer in PP/ poly(vinyl chloride) (PVC) blends was also examined. In comparison with PP/PVC blends, the average size of the dispersed phase was greatly reduced in grafted polypropylene (gPP)/PVC blends because of the addition of the PP-*g*-(St-*co*-MMA) graft copolymer. The tensile strength of the gPP/PVC blends increased significantly, and the impact strength was unchanged from that of the pure PP/ PVC blends. The results of differential scanning calorimetry and scanning electron microscopy suggested that the compatibility of the PP/PVC blends was improved. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 2356–2363, 2008

Key words: blends; compatibility; graft copolymers; poly (propylene) (PP); poly(vinyl chloride) (PVC); compatibility

INTRODUCTION

Incompatible polymer blends exhibit coarse phase morphologies and poor mechanical properties, which are undoubtedly attributable to the high interfacial tension and the lack of adhesion at the interface between the phases associated with their incompatibility. To reduce the interfacial tension and improve the adhesion between different phases, one of the most efficient methods is to add preformed block or graft copolymers used as compatibilizers to the blends.[1,2]

Graft copolymers of polypropylene (PP) have bee widely used as compatibilizers in blends of PP with other plastics such as polyamides and polyesters, which are generally produced by melt free-radical grafting of monomers onto PP chains. Various monomers have been used for melt-grafting reactions. The most commonly employed monomers are maleic anhydride, glycidyl methacrylate, and vinyl and acrylic monomers containing reactive functional groups.[3]

However, the grafting yields of those monomers are usually low, and the PP matrix undergoes β-scission-induced PP chain degradation in the course of grafting the polar monomer.[4–6] To obtain high grafting yields and reduce side reactions, it is essential that the macroradicals react with the grafting monomer before they undergo side reactions. Recently, a so-called comonomer concept has been developed to improve the grafting yields of glycidyl methacrylate onto PP and polyethylene.[6,7] The idea of using a comonomer is associated with the commonly accepted fact that a free-radical process starts with the formation of macroradicals along the polymer chains by a so-called hydrogen-abstraction mechanism. These macroradicals might subsequently follow two competing pathways. They could either initiate the grafting of the monomer or undergo chain scission. The latter depends on the nature of the polymer backbone deeply. In the case of PP, the main side reaction is β-scission associated with PP macroradicals,[6] which causes a reduction in the molecular weight of the polymer.

Styrene (St) has been found to be a good comonomer to promote melt free-radical grafting and reduce the chain scission of the PP matrix. That is believed to be related to the high reactivity toward PP macroradicals

Correspondence to: G. Yang (ygs20002000@yahoo.com).

and the stability of the resulting product. St reacts rapidly with PP macroradicals, and the resulting styryl macroradicals copolymerize readily with the grafting monomer.[4,6,8]

The objective of this study was twofold: to provide a detailed investigation of the melt free-radical grafting of methyl methacrylate (MMA) onto PP with St as a comonomer in a single-screw extruder and to study its ability to compatibilize incompatible blends. Specifically, the multimonomer-grafted polymer PP-g-St-co-MMA was synthesized. Additionally, poly(vinyl chloride) (PVC) has strong polarity and highly retarding combustibility; PP has no polarity and good fluidity. Because of the mutual supplement in the two polymers, PP/PVC blends were selected for study; they can reduce the halogen content of PVC and increase the scratch resistance of PP. Subsequently, grafted polypropylene (gPP) was directly blended with PVC and compared with the PP/PVC blends. The mechanical proprieties, thermal behavior, and morphology of the blends were investigated in detail. This article also reports a new way to improve the poor compatibility of the reversed polar polymers and more reasonable applications of recycled PVC.

EXPERIMENTAL

Materials

The PP and PVC used in this study were commercial products: the former (T30S) was supplied by Daqing Petrochemical Factory (Heilongjiang, China) with a melt flow rate (MFR) of 3.5 g/10 min; the latter (SGS-6) was a product of Baoding Electrochemical Plant (Hebei, China). The grafting monomers were MMA (Xintong Fine Chemical Co., Ltd., Tianjin, China) and St (Fuxing Chemical Factory, Beijing, China). Dicumyl peroxide (DCP) was chosen as an initiator and was purchased from Shanghai Chemical Reagent Co. (Shanghai, China); it was a saturated water solution (concentration = 50%).

Preparation and purification of multimonomer-grafted PP

The radical initiator, MMA, and St were introduced into a beaker first. The resultant mixture was dry-blended with PP pellets before being charged into the extruder at room temperature for about 30 min so that they could be absorbed by the PP matrix. Then, the reactions of melt-grafting St and/or MMA onto PP were carried out in a single-screw extruder (type XJ-20, Scientific Research Instrument Factory, Jilin University, Jilin, China). The screw diameter was 20 mm, and the screw diameter-to-extruder length ratio excluding the die was 20. The extruding temperature was set in the range of 160–210°C.

The crude grafted samples were first dissolved in hot toluene and then precipitated in excess acetone at room temperature; gPP and pure PP were precipitated, whereas homopolymers and copolymers, such as poly(methyl methacrylate) (PMMA), polystyrene (PSt), and poly(styrene-co-methyl methacrylate), remained soluble. After that, the precipitated samples were filtered and dried in vacuo at 80°C for 12 h.

Characterization of modified PP

Fourier transform infrared (FTIR) spectroscopy was carried out with an FTS-40 spectrometer (Bio-Rad Co., CA) between 4000 and 500 cm^{-1} with a resolution of 2 cm^{-1} at room temperature, which was used to determine the grafting yields of MMA and/or St onto PP.

MFR measurements of the purified PP samples were carried out with a μPXRZ-400C melt indexer (Jilin University Scientific Research Instrument Factory, Jilin, China) at 230°C with a load of 2.16 kg according to ASTM Standard D 1238.

Measurements of the mechanical properties of the blends

PVC with its processing agent at a fixed ratio was first dry-mixed by a high-speed mixer, and this was followed by melt blending in a two-roll mixing mill for plastics (XKR-160, Zhanjiang Machine Co., Guangdong, China) for plasticization for 4 min, and the plasticization of PP or gPP followed the same procedure used for PVC. PVC was added to plasticized PP or gPP, and this was followed by blending for another 4 min. After that, the blends were compressed into sheets with a hydraulic press at 180°C and 10 MPa for 5 min, and they were designated PP/PVC or gPP/PVC. Before each processing step, all the sheets were dried in a vacuum oven at 80°C for 12 h. The notched Izod impact strength was measured with an XCJ-40 impact tester (Chengde Laboratory Instrument Works, Hebei, China). Tensile testing was performed on an LJ-500N tensile test machine (Chengde Laboratory Instrument Works) at a speed of 10 mm/min.

Differential scanning calorimetry (DSC) investigation

DSC measurements were carried out on a DT-40 modulated differential scanning calorimeter (Shimadu, Kyoto, Japan) calibrated by indium standards. All the measurements were performed from room temperature to 200°C at a heating/cooling rate of 20°C/min under a nitrogen atmosphere and maintained at that temperature for 5 min to eliminate any
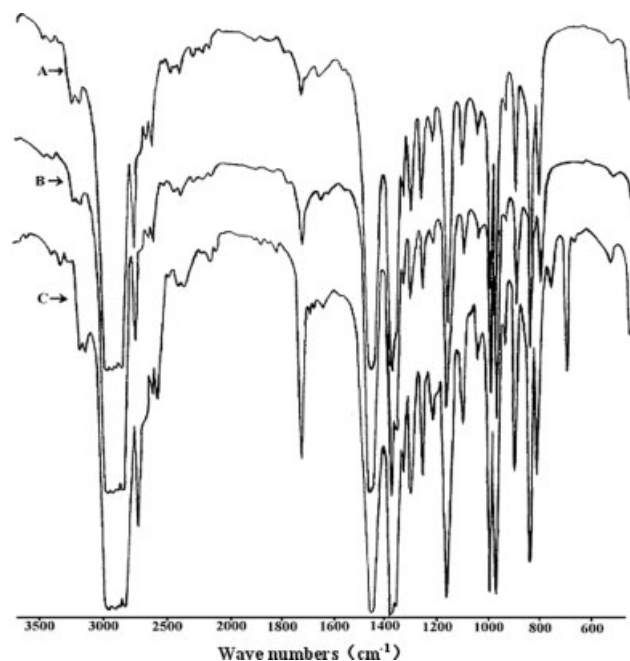
Figure 1 FTIR spectra of (A) pure PP, (B) PP-*g*-MMA, and (C) PP-*g*-(St-*co*-MMA).

previous thermal history. The glass-transition temperature (T_g) was determined in the second heating scan.

Blend morphology

The cryofractured surfaces of all samples were characterized with a KYKY-1000B scanning electron microscope (Beijing Analytic Instrument Co., Ltd., China) operated at 15 kV. The specimens were immersed in liquid nitrogen for 5 min and then fractured. The fractured surfaces after proper drying were sputtered with a thin layer of carbon before scanning electron microscopy (SEM) examinations.

RESULTS AND DISCUSSION

FTIR analysis of PP-*g*-(St-*co*-MMA)

The FTIR spectra of pure PP, PP-*g*-MMA, and PP-*g*-(St-*co*-MMA) are shown in Figure 1. The characteristic absorption peaks at 1730 cm^{-1} corresponded to the absorption of the carbonyl groups of MMA. The peaks at 700 and 2720 cm^{-1} were attributed to the characteristic absorptions of the St and PP skeleton, respectively. The aforementioned results illustrated that both MMA and St were grafted onto PP.

To obtain the quantitative results, the FTIR absorbance ratio technique was applied to determine the grafting yields.[4,9,10] The absorption peak at 2720 cm^{-1} was chosen as an internal reference, and that at 1730 cm^{-1} was used to determine the grafting degree of MMA. The peak at 700 cm^{-1}, correspond-
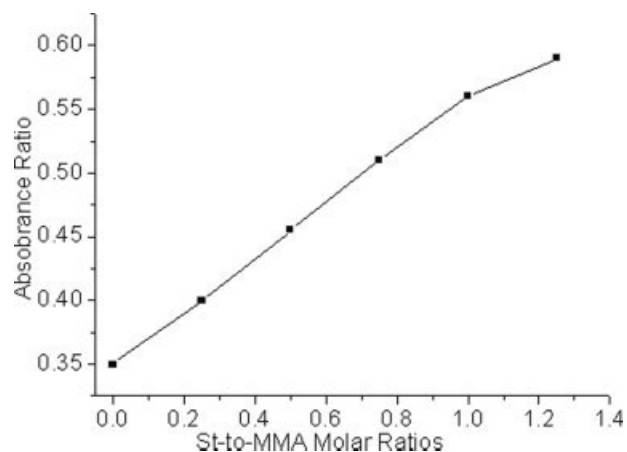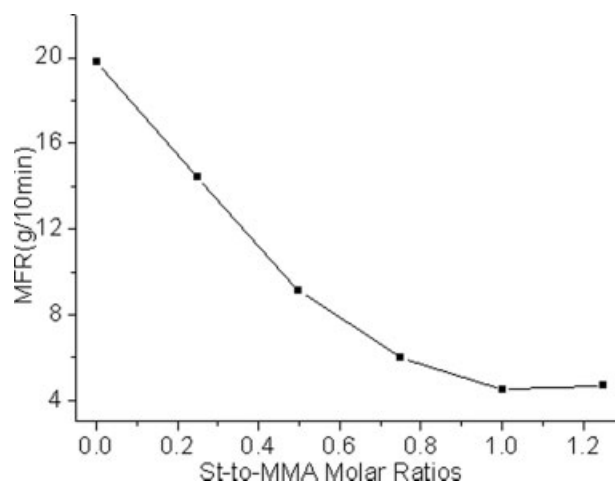

Figure 2 Effect of the monomer molar ratios on the grafting degree of gPP.

ing to the stretching of the hydrogen atoms of the monosubstituted aromatic ring of St, was chosen for measuring the amount of grafted St. The relative absorbance ratio (RAR) values of the areas of the peaks at 1730 (or 700) and 2720 cm^{-1} showed the relative grafting degree of MMA (or St).

Preparation and characterization of PP-*g*-(St-*co*-MMA)

The important contribution of using St as a comonomer to enhance MMA grafting yields and to reduce β-scission-induced PP chain degradation is illustrated in Figures 2 and 3.

Figures 2 and 3 show the RAR and MFR values as a function of the [St]/[MMA] molar ratio for a given concentration of charged MMA (6.0 phr), respectively. As shown in Figure 2, in the absence of St, the RAR value, which was a delegate to the grafting degree of MMA, was very low because of the low
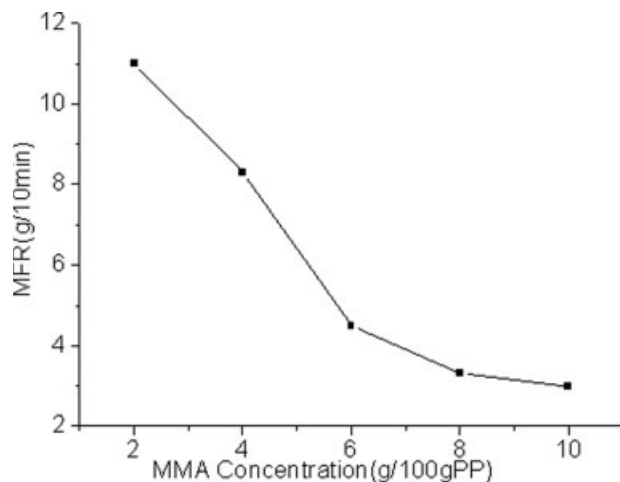

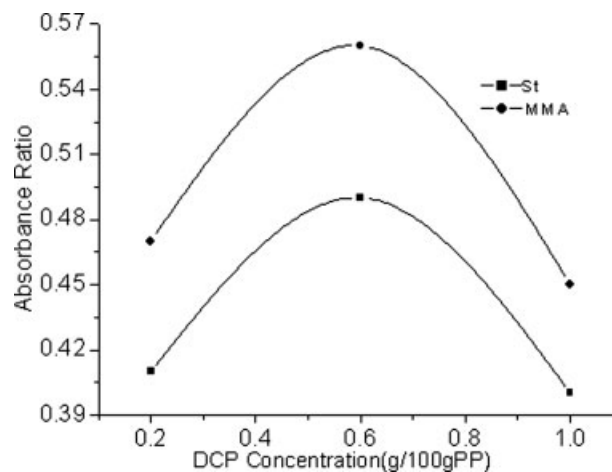**Figure 3** Effect of the monomer molar ratios on the MFR value of gPP.
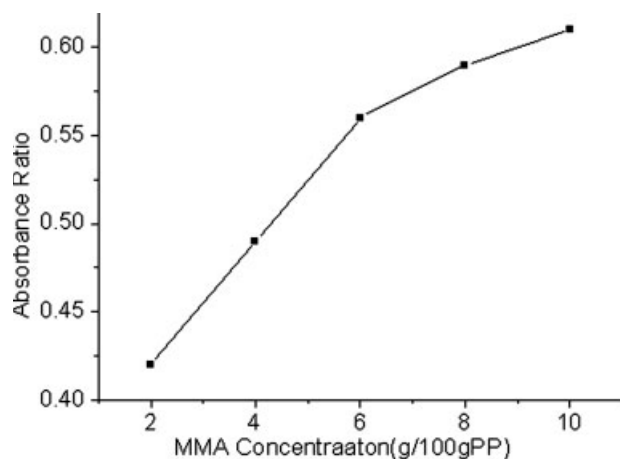
Figure 4 Effect of the MMA concentration on the grafting degree of gPP.

Figure 6 Effect of DCP on the grafting degree of gPP.

reactivity of MMA. With St added as a comonomer, the RAR values linearly ascended with an increasing molar ratio of the two monomers until the ratio was 1 : 1; in succession, the change became slow. This might have been caused by the greater and greater amounts of homopolymers and copolymers,[6] such as PMMA, PSt, and PSt–PMMA; all these byproducts were obtained with the grafting reaction. When the molar ratio was small, the grafting reaction was dominant; all aforementioned side reactions were negligible. With the molar ratio increasing, especially beyond 1 : 1, these side reactions affected the grafting yields, which declined to a large degree. The RAR values of MMA, on the other hand, always were larger than those of St. It was a interesting phenomenon to notice for us because of the higher reactivity of St versus that of MMA. As shown in Figure 3, the MFR value decreased drastically from 19.8 to 4.6 as the molar ratio increased to 1 : 1 and then leveled off.

For a given condition, the DCP concentration and the [St]/[MMA] molar ratio were fixed at 0.6 phr and 1 : 1, respectively. Figure 4 shows that the higher the monomer concentration (MMA or St) was, the higher the RAR values were of MMA and St. Figure 5 shows the effect of the grafting monomer concentration on the MFR values of gPP obtained under the same conditions used for Figure 4. The MFR values of gPP decreased with increasing monomer concentration, and some were similar to those of pure PP; this meant that the addition of St reduced the degradation of PP effectively.

From Figures 3 and 5, it is clear that the degradation of PP chains was reduced significantly with the addition of St; otherwise, the ability of St to promote the MMA grafting yields might be obtained from Figure 4. In other words, to a great extent, the comonomer St could reduce β-scission of the PP matrix and enhance the grafting efficiency.

To investigate the influence of DCP on the grafting degree and MFR values of gPP, the monomer molar

Figure 5 Effect of the MMA concentration on the MFR value of gPP.
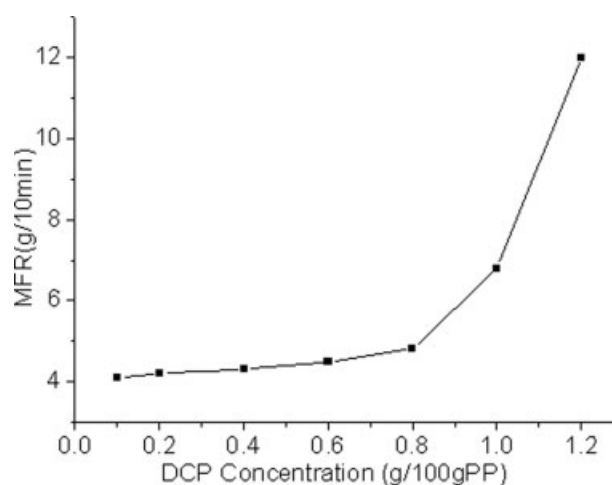
Figure 7 Effect of DCP on the MFR value of gPP.

TABLE I
Mechanical Properties of Pure PP, PVC, gPP, and Their Blends

PP (g)	PVC (g)	gPP (g)	Tensile strength (MPa)	Impact strength (kJ/m²)
0	100	0	45.0	—
100	0	0	35.2	2.01
0	0	100	34.7	1.78
20	80	0	9.2	1.60
40	60	0	9.4	1.45
60	40	0	22.7	1.48
80	20	0	28.1	1.75
0	80	20	20.0	1.63
0	60	40	7.6	1.66
0	40	60	23.6	1.69
0	20	80	34.3	1.80

ratio was fixed at 1 : 1, and the contents of the two grafting monomers were both 6 phr with respect to PP. It can be seen from Figure 6 that the changes in the RAR values were large. In the initial time, because most DCP was consumed by the grafting reaction, RAR increased significantly and reached a peak value at 0.6 phr DCP. However, Figure 7 shows that the MFR values changed little when the content of DCP ranged from 0.2 to 0.8 phr. When the content of DCP increased consecutively, the RAR values decreased rapidly and the MFR values increased; the greater the DCP concentration was, the greater the decrease was of the RAR values and the greater the increase was of the MFR values. This might be related to the greater degradation of the PP matrix. Therefore, the surplus of DCP content was harmful to the graft reactivity. Additionally, the RAR values of MMA were higher than those of St and no longer limited by a plateau; instead, they increased with an increasing initial concentration of MMA. Similar phenomena have been found for other grafting systems.[6–8,11] As a result, St as a comonomer could pro-

vide additional freedom in controlling different monomers' grafting yields in some systems.

Mechanical properties of the PP/PVC and gPP/PVC blends

As we all know, PP and PVC are two kinds of important plastics, and they are widely used in many fields. Because of their different polarities, poor adhesion, and high interfacial tension, they are incompatible. Thus, a corresponding blend possessing useful properties cannot be obtained by direct blending of the two polymers, and there are only a few reports on the subject.[12–15] In this study, the multimonomer-grafted PP as a compatibilizer was directly added to PVC, and a systematic study was performed.

Table I summarizes the mechanical properties of gPP/PVC blends with different proportions. In addition, the mechanical properties of PP/PVC binary blends are given for comparison. Although the tensile strength of pure PVC (45.00 MPa) was higher than that of PP (35.17 MPa), the tensile strength of PP/PVC blends significantly decreased with the PVC content increasing. Therefore, it was impossible to obtain a good material by direct melt blending of PP and PVC. However, the tensile strength of gPP/PVC blends increased to a significant degree, except for the 40/60 weight ratio of gPP/PVC. In other words, the multimonomer-grafted PP could improve the compatibility of the PP/PVC blends and enhance the tensile strength, whereas phase inversion played a major role with the 40/60 weight ratio of gPP/PVC. The impact strength of gPP/PVC was
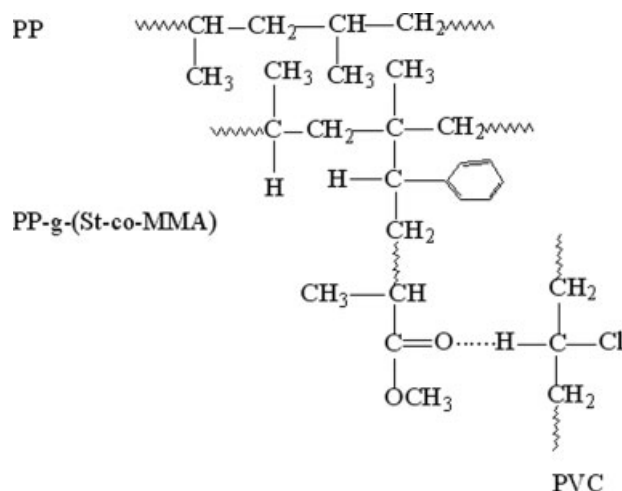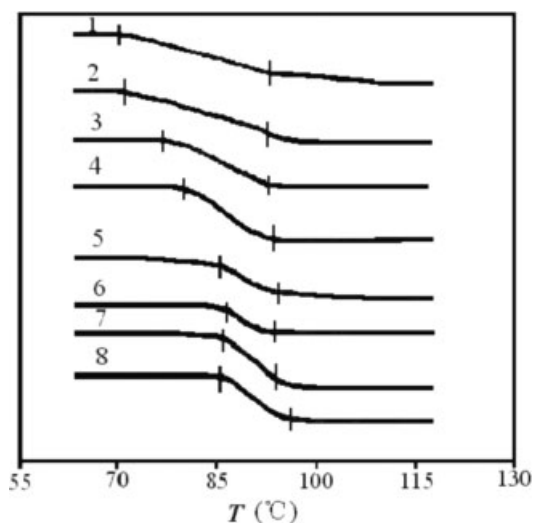

Figure 8 Compatibilization scheme of PP/PVC by PP-g-(St-co-MMA).

TABLE II
Effect of the gPP or PP Contents on T_g of PVC in gPP or PP/PVC Blends

Weight ratio of PP (or gPP)/PVC blends	80/20	60/40	40/60	20/80
$T_{g(PVC)}$ of PP/PVC (°C)	88.7	89.2	90.1	90.4
$T_{g(PVC)}$ of gPP/PVC (°C)	77.9	79.1	84.3	86.0

Figure 9 DSC melting endotherms of gPP/PVC and PP/PVC blends with different weight ratios: (1) 80/20, (2) 60/40, and (3) 40/60, and (4) 20/80 gPP/PVC and (5) 80/20, (6) 60/40, (7) 40/60, and (8) 20/80 PP/PVC.

unchanged from that of PP/PVC over the entire study range.

Furthermore, as shown in Figure 8, gPP contained C=O groups, which existed in the phase interfaces of the blends and could form hydrogen bonds with hydrogen atoms of PVC; this could reduce the interfacial free energy and the interfacial tension and increase the adhesion between two different phases. On the other hand, because of the similarity of the dissolubility parameters (δ) for PVC (δ = 19.0–22.1) and PMMA (δ = 19.0),[16] according to the principle, the polymers might be compatible if they had similar δ values. Thus, the MMA chain diffused toward the PVC matrix; the PP chain grafted MMA and/or St monomers in gPP can form crystal together with those pure PP chain so that could assume the most optimum conformations at the interface and play its compatibilizing role in full.[17] In fact, the grafted polymer acted as an anchor at the interface of PP and PVC.
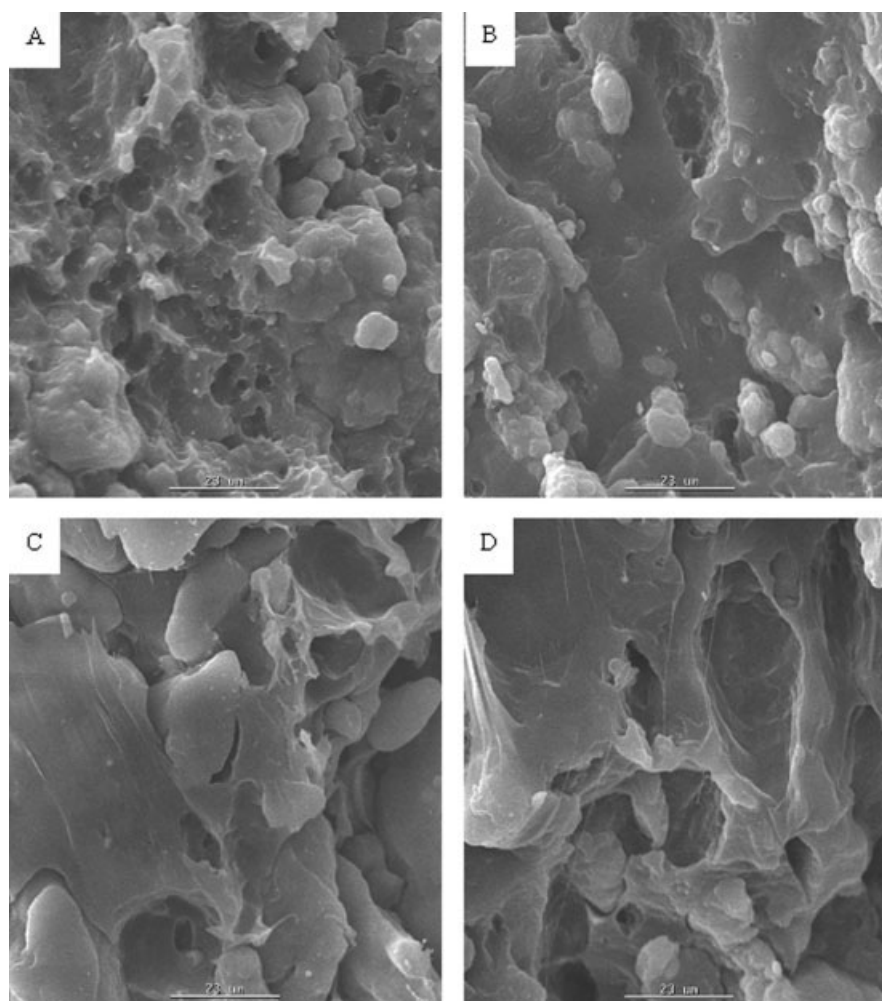
Figure 10 SEM micrographs of the fractured surfaces of PP/PVC blends with weight ratios of (A) 20/80, (B) 40/60, (C) 60/40, and (D) 80/20.

DSC investigation

Table II presents the T_g values of the PVC portion in the two different blends, which are denoted $T_{g(PVC)}$. Because of the poor compatibility of PP and PVC, the $T_{g(PVC)}$ values (ca. 90°C) were almost independent of the weight ratio of the PP/PVC blends. However, with the addition of gPP to PVC, it was not difficult to find that all the $T_{g(PVC)}$ values decreased and tended toward that of PP (-14°C). When the gPP/PVC weight ratio was 80/20, the $T_{g(PVC)}$ value decreased about 11°C. Meanwhile, as can be seen in Figure 9, the $T_{g(PVC)}$ range became wide with the addition of gPP. The more gPP was added, the wider the $T_{g(PVC)}$ range became. All this shows that gPP improved the compatibility of the PP/PVC blends to a certain extent.

Blend morphology

The morphologies of gPP/PVC blends with four different weight ratios were selected as examples in contrast to PP/PVC blends to examine the effect of PP-*g*-(St-*co*-MMA) on the compatibility between PP and PVC. Figure 10 shows SEM micrographs for the cryofractured surfaces of PP/PVC binary blends. As expected, the PP/PVC blends exhibited a distinctly two-phase structure because of their poor compatibility. The morphology was irregular, containing spherical particles, and the interface was clear with a little cohesion.

However, Figure 11 shows a marked difference in the gPP/PVC blends with respect to the morphology. It was easy to find that the dispersed phase was smaller and the size distribution was more uniform; the hole that was pulled out from the fracture
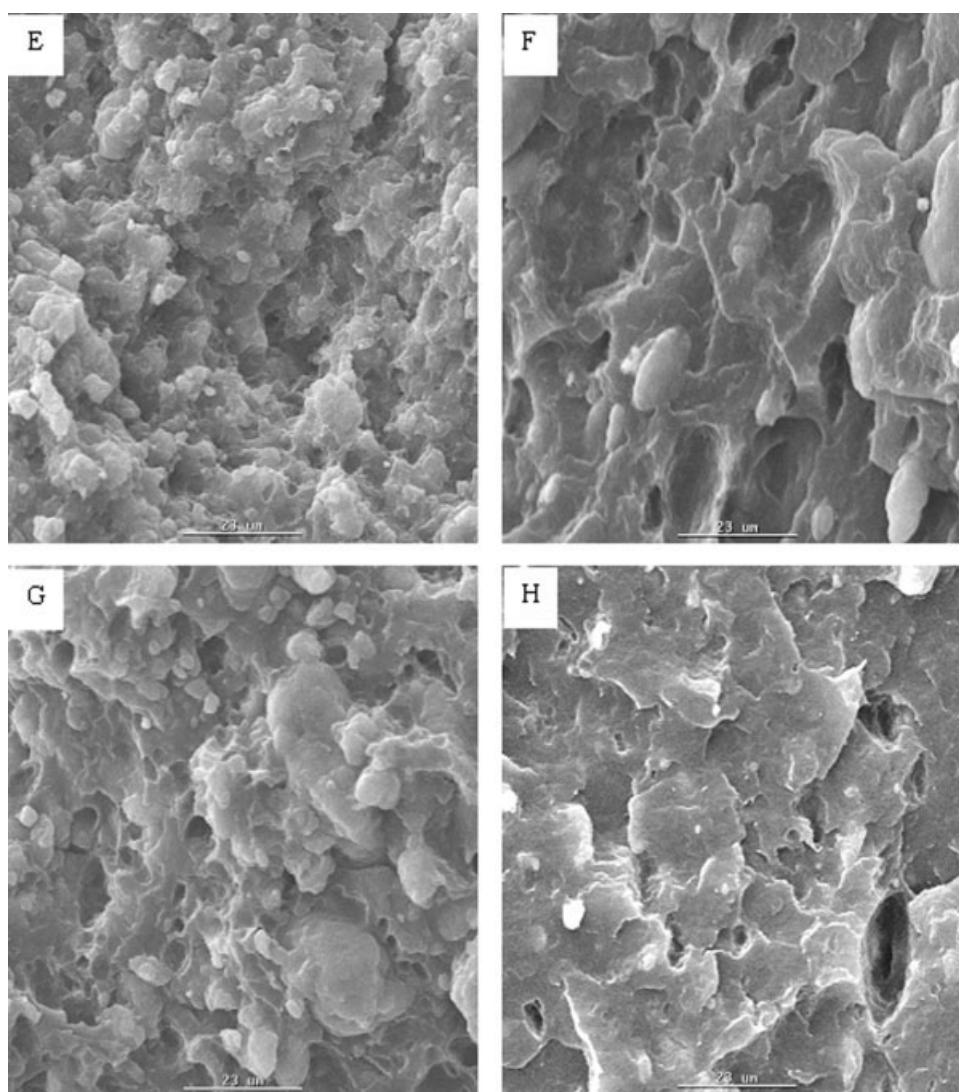
Figure 11 SEM micrographs of the fractured surfaces of gPP/PVC blends with weight ratios of (E) 80/20, (F) 60/40, (G) 40/60, and (H) 20/80.

surface was indistinct and white in the gPP/PVC blends. The SEM results showed clearly the effect of PP-*g*-(St-*co*-MMA) on the compatibility of the PP/PVC blends. These results all well agreed with those the aforementioned tests.

CONCLUSIONS

Multimonomer melt grafting onto PP was successfully performed in one step in a single-screw extruder and was characterized by means of FTIR and MFR. The effects of the monomer molar ratio, the monomer concentration, and the initiator concentration on the grafting reaction were investigated in detail. It was shown that the addition of St as a comonomer to the melt-grafting system could significantly enhance the grafting degree of MMA onto PP and reduce the chain scission of PP. The maximum MMA grafting degree was obtained when the [St]/[MMA] molar ratio was approximately 1 : 1; and the MFR value of gPP was lowest in this case, too. As a compatibilizer, the multimonomer-grafted PP was used in PP/PVC blends. In comparison with PP/PVC blends, the tensile strength of gPP/PVC blends was increased significantly with impact strength maintenance, except for the phase-inversion regions. Moreover, the T_g values and morphologies, which were obtained from DSC and SEM investigations, respectively, indicated that PP-*g*-St-*co*-MMA improved the compatibility between PP and PVC.

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