

A Facile, Green, Versatile Protocol to Prepare Polypropylene-*g*-Poly(methyl methacrylate) Copolymer by Water-Solid Phase Suspension Grafting Polymerization Using the Surface of Reactor Granule Technology Polypropylene Granules as Reaction Loci

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ABSTRACT: A facile and environment friendly process, called water-solid phase suspension grafting polymerization, was developed to prepare polypropylene-*g*-poly(methyl methacrylate) (PP-*g*-PMMA) copolymer with a submicrometer microdomain. In this approach, graft polymerization was elaborately regulated to occur within micropores of polypropylene particles prepared by reactor granule technology. FTIR spectra of the samples after extraction demonstrated that PMMA was successfully grafted onto the PP. The results showed grafting percentage (GP) of PMMA increased with the increasing monomer ratios to PP and that could reach 13.6%. Whereas the grafting efficiency decreased as the monomer ratio increased. The addition of second monomer styrene improved GP up to 24.5%. Differential Scanning Calorimetry tests showed that the grafting of PMMA have a slight effect on the melting point and the relative crystallinity of PP. TEM micrographs demonstrated PMMA domains distributed in PP matrix with sizes ranging from about 100 to 300 nm. In addition, Shear viscosity increased with the growing GP indicated by rheological measurement. The preliminary evaluation showed PP-*g*-PMMA was effective in improving the compatibility of PP/acrylonitrile-styrene-acrylate blends. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 3170–3177, 2013

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INTRODUCTION

As a thermoplastic polymer, polypropylene (PP) is used in a wide variety of applications, including packaging, household electrical appliances, chemical machinery, and power transportation, as a result of its outstanding physical, chemical, mechanical, and thermal properties. However, the nonpolar nature makes PP exhibit poor adhesion, dyeing, antistatic performance, and poor compatibility with other polymers.^{1,2} Although there have already been many efforts of physical and chemical approaches to overcome the drawbacks mentioned above, the most commercially effective method is grafting polymerization modification. Depending upon the final application, there are two main grafting processes. Surface grafting is aimed at modifying the surface properties of PP articles, and bulk grafting polymerization is for preparing new PP-based functional resins, modifiers, and copolymers.

Up to now, many strategies have been developed to prepare PP-based graft copolymers. For bulk PP resin modification, the

established approaches include melt,^{3–7} solution,^{8,9} solid phase,^{10,11} and liquid–solid phase suspension grafting.^{12–15} Melt grafting can be performed in an extruder or an internal mixer and is used extensively in industry and the laboratory. However, it also suffers from significant disadvantages, e.g., low grafting efficiency, PP β -chain scission, initiator/monomer residue, and high energy consumption. Solution grafting is usually carried out in a solution of PP, initiator, monomer, and solvent under the reaction temperature of 100–140°C. Although the homogeneous phase is beneficial to grafting polymerization and the lower reaction temperature decreases degradation, the environmental pollution caused by organic solvent presents an unavoidable new problem. Solid phase grafting is usually performed with PP powder as raw material in the presence of an initiator and monomer mixture, and a little cosolvent is employed if necessary. However, the grafting polymerization only takes place on the surface of the PP powder particles, so the ratio of the graft copolymers to PP depends greatly on the particle size of

PP powder. Moreover, the separation of the unreacted monomer, solvent, and homopolymer significantly complicates the preparation process.

In the history of PP industry, Reactor Granule Technology (RGT) could be featured as a significant advancement.^{16–20} Based on the growth mechanism, the end-product PP nascent resins consist of agglomerated submicroparticles (about 0.5 μm in diameter). Moreover, the very important characteristic of RGT PP is its controlled high porosity (from 10 to more than 40 vol %). In principle, the porous PP granules can act as reactors to perform free radical polymerization. However, because it is only simple “filling polymerization”, desired composite materials or alloys still cannot be obtained because of the incompatibility of PP with most other polymers. Fan and coworkers^{21–26} reported the solid-phase grafting in the pores and surface of self-prepared spherical PP granules via RGT by using a peroxide initiator under the temperature of 130°C. The grafting percentage (GP) and grafting efficiency (GE) of the products are 15–24.3% and 42–56.7%, respectively, which implied that products are a mixture of homopolymers and grafting polymers at a nearly equal level. Therefore, it undoubtedly will be a significant progress if effective graft polymerization can be conducted in porous PP granules. This not only will extend RGT from Ziegler-Natta polymerization to free radical polymerization, but also will develop a series of novel high-performance functional PP resins and copolymers.

Based on the systematic and continuous researches on surface grafting polymerization in our laboratory, we developed a facile and environmentally friendly approach to graft vinyl acetate onto low-density polyethylene films in aqueous solution with benzoyl peroxide (BPO) as initiator.²⁷ The key mechanism of this method was surface abstracting hydrogen (chain transfer) reaction of phenyl radicals from BPO decomposition. It was concluded that the heterogeneous interface affect not only promoted benzoyl free radicals to further decompose into phenyl radical, but also was beneficial to the chain transfer reaction between the nonpolar phenyl radical and the surface-H on the plastic substrate. As a successful extension of that work, we herein present a very efficient, environmentally friendly and versatile strategy called water-solid phase suspension grafting polymerization (WSGP) to prepare PP-based functional graft copolymers. In this article, the nascent porous PP particles were firstly immersed in a solution of BPO/acetone, and then suspended in a mixture of methyl methacrylate (MMA) and water. Finally the WSGP was performed with the application of stirring and heating. After polymerization, graft copolymer particles are suspended on the surface of the reaction medium (water solution). Thus it was very simple to separate product, and the remained graft solution could be re-used.²⁸ The final product was still in the form of regular spherical granules.

EXPERIMENTAL

Materials

Commercial PP spheres, T30S, were provided by Sinopec Jinan Petrochemical Company Limited. The melt flow index (MFI) is 3.95 g·10 min⁻¹ measured at 2.16 kg at 230°C. MMA and styrene are analytical grade reagents bought from Beijing Yili Fine

Chemicals Corporation and were vacuum-distilled before using. BPO, C.P. grade, purchased from Beijing Chemical Reagents Company, had been purified by recrystallization in ethanol before using. Irganox 1010 and Irganox 168 were used as received. Acrylonitrile-styrene-acrylate (ASA) copolymer, 978DB, was bought from LG Chemical.

Procedures of Grafting Polymerization

Grafting polymerization was carried out in a 500-mL three-necked round-bottom flask equipped with an overhead mechanic stirrer, a nitrogen purging inlet and a condenser. Typically, a certain amount of BPO was dissolved in acetone, and then the solution was soaked into PP spheres. After about 30 min the PP was dried in an exhaust hood and BPO was coated onto the surfaces of the PP particles. Then monomer MMA was mixed with the PP particles coated with BPO and stood for about 10 min. About 200 mL DI water was poured into the flask and purged with nitrogen when it is up to the setting temperature of 80°C. Then the mixture (PP particles soaked with BPO and MMA) was added into the reactor. The grafting polymerization was preceded at the constant temperature for about 2.5 h with gentle nitrogen flow. After polymerization the reactants were filtered and then grafted PP spheres were extracted with acetone in a Soxhlet extractor for 24 h and dried to the constant weight *in vacuo* at 50°C. The GP and GE were calculated as per the following equations:

$$\text{GP} = (W_1 - W_0)/W_0 \times 100 \quad (1)$$

$$\text{GE} = (W_1 - W_0)/(W_2 - W_0) \times 100 \quad (2)$$

where W_0 is the mass of blank PP spheres, W_1 is the mass of grafted PP spheres after extraction, and W_2 is the mass of PP spheres before extraction. Data of PP grafting PMMA are summarized in Table I.

Fourier-Transform Infrared (FT-IR) Spectroscopy of PP-g-PMMA

The samples for FT-IR analysis were prepared by melting casting a thin graft polymer film on the potassium bromide (KBr) pellets held by a heated sample fixture. The FT-IR spectra of PP-g-PMMA were recorded with a Nicolet NEXUS 670 FT-IR spectrometer.

MFI of PP-g-PMMA

To reduce the degradation of PP at high temperature, about 0.1-g antioxidants (Irganox 1010 and Irganox 168, in 2:1) were dissolved in 10-mL acetone and then mixed with about 50 g grafted PP spheres. Then the mixtures were stirred for 5 min and dried in an exhaust hood at ambient. The MFI was measured at 2.16 kg at 230°C with a XNR-400 instrument manufactured by The Second Testing Machine Company (Changchun) Limited.

Morphology of PP-g-PMMA

Scanning electron micrographs (SEM) were obtained using a Hitachi S-4700 SEM instrument. TEM observations were performed with a HITACHI H-800 transmission electron microscope at an acceleration voltage of 200 kV and at a magnification of 10⁴ and 5 × 10⁴ respectively. The ultrathin sections were cut by a Leica EM FC6 Ultra microtome equipped with a glass

Table I. The Summary of the PP-g-PMMA Experiments

RUN	PP (g)	St (g)	MMA (g)	BPO (g)	GP (%)	GE (%)	ΔH_m (J·g ⁻¹)	T_m (°C)
0	50	0	0	0	0	0	97.28	163.03
1	50	0	2.36	0.25	2.2	78.01	92.84	163.08
2	50	0	4.72	0.50	5.3	80.21	85.90	162.74
3	50	0	7.08	0.75	7.5	72.29	81.36	161.68
4	50	0	9.44	1.00	9.3	67.70	81.40	162.97
5	50	0	11.80	1.25	11.3	61.61	76.98	161.13
6	50	0	14.16	1.50	13.6	61.83	74.17	160.54
7	50	4.53	9.44	0.30	16.9	74.92	N/A	N/A
8	50	9.05	18.88	0.60	24.5	49.54	N/A	N/A
9	50	13.58	28.32	0.90	19.4	25.69	N/A	N/A

N/A, Not available.

knife at a low temperature and chemically stained in ruthenium tetroxide (RuO₄) vapor.

Differential Scanning Calorimetry of PP-g-PMMA

Thermal analysis was performed with a Q100 DSC of TA, USA, with Refrigerated Cooling System 90 and a Universal Analysis 2000. The samples were first annealed at 200°C for 3 min to eliminate any thermal history and cooled to room temperature at -60°C·min⁻¹. The thermogram of each sample was recorded in the second cycle with a heating rate of 10°C·min⁻¹ from 40°C to 200°C.

Rheological Properties of PP-g-PMMA

Dynamic rheology experiments were performed with a controlled strain Rheometer (ARES, TA Instruments) having 25 mm parallel plates with a gap of 0.3 mm. Disks of the composites (25 mm diameter, 1 mm thickness) for rheological measurements were prepared using compression molding at 170°C. Data were collected over a frequency from 0.05 to 100 rad·s⁻¹ at a constant temperature of 200°C, and the applied strain amplitude was 3%. Both nitrogen atmosphere and antioxidants (0.2 wt % of PP, m₁₀₁₀/m₁₆₈ = 2:1) were used to prevent sample degradation.

PP-g-PMMA as Compatilizer of PP/ASA Blend

The process of blending and kneading was carried out in a Thermo HAAKE PolyLab System (Rheomix 600p) using a 69-mL mixing bowl at a temperature of 180°C for 12 min at a speed of 60 rpm. The morphology of the blends was observed by a HITACHI S-4700 SEM.

RESULTS AND DISCUSSION

Grafting Sites and Mechanism for the Surface Grafting Polymerization

The purpose of this investigation was to exploit the grafting polymerization within micropores inside the PP granules. Before the reaction, BPO and MMA diffused into the pores of PP particles with the help of capillary adsorption. Patel et al.²⁹ investigated the swelling capability of many monomers of PP and pointed out that MMA was not a good swelling monomer for PP. Even so, the sorption of MMA in PP was determined to be 16.3% because of the porosity of PP. And stirring made the PP particles separate from each other; therefore each particle was

equivalent to an independent reaction bed sealed by the hot water. So it was difficult for hydrophobic MMA to transfer into water during the grafting process. When heated, BPO firstly decomposed into benzoyl free radicals. According to our experimental setup, BPO was mainly located on the outer surface of PP and the inner-pore surface or the interface between the PP and monomer. The environment of BPO was quite different from when it was surrounded by a solution. Therefore it had enough time for benzoyl free radicals to take a further decomposition into phenyl radicals because of space limitation. The authors believe that the strong hydrogen abstraction ability of phenyl radical from PP surface is a key to get high graft efficiency in this system. The enclosed reactor could not only decrease the diffusion and overflow of phenyl radical, but also promote the chain transfer reaction between phenyl radical and the surface-H on the similarly lipophilic PP substrate. There were three competitive reactions among these radicals, adding to the monomer to form growing chains, abstracting hydrogen atom from the PP surface to form the macromolecular radicals and terminating with another free radicals. During whole grafting process, if the termination is not the main reaction for these free radicals, a high-efficiency grafting can be performed accordingly. Considering the polymerization, temperature (80°C) was much lower than the PP melting point the grafting polymerization was mainly taken place in these microbulk reactors. Limited by the small space, the homopolymer chain free radical might couple with a surface grafting chain free radical resulting in increase of both GP and GE. With the proceeding of the polymerization, monomers absorbed on the outside of the PP granules could diffuse into the micropores driven by the volume shrinkage of the grafting polymerization.

The unique character of the PP granules by RGT is that the particles are consisted with the submicrometer nuclei or submicroparticles.^{23,30} Figure 1 shows the SEM images of PP granules before and after grafting PMMA. The PP granule [Figure 1(A)] consists of subparticles with the diameter about 500 nm. Although some fibril polymers can be observed, the subparticle structure is really clear. After grafting polymerization with PMMA [Figure 1(B, C)], it could be observed that some fibril polymers attach to the shell of the PP subparticles and diffuse

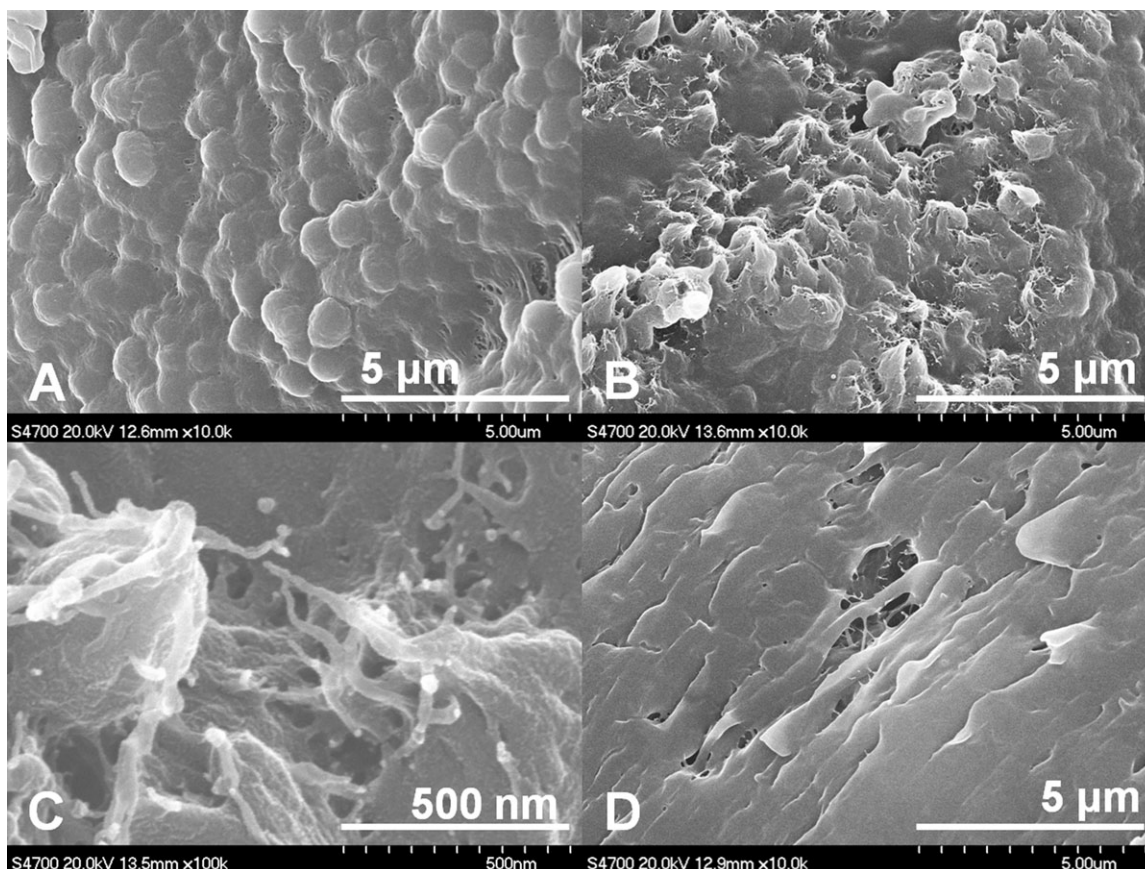


Figure 1. SEM images of PP granules before and after grafting PMMA (Run 6, in Table I). (A) Microparticle in nascent PP granules. (B) Interior of PP-g-PMMA before being extracted with acetone (magnification of 10^4). (C) Interior of PP-g-PMMA before being extracted with acetone (magnification of 10^5). (D) Interior of PP-g-PMMA after being extracted with acetone.

into the pores among the subparticles. This showed the grafting and/or homopolymerization of MMA could be introduced in the micropores inside PP granules. More interestingly, the grafting polymers dispersed finely among the subparticles of PP that is very helpful in the preparation of PP-based copolymers. The immiscible PP and PMMA chains usually cannot achieve this good dispersion observed in SEM images that is difficult for the traditional nonporous PP resins. In the PP-g-PMMA copolymers, the graft-PMMA and homo-PMMA do not fill the whole micropores of PP, and acetone is a good solvent of PMMA [Figure 1(B)]. Therefore the long and rigorous extraction can remove the PMMA homopolymers completely.³¹ Figure 1(D) shows the SEM image of the grafting product extracted in acetone for 24 h. According to the picture, fibril polymers become a smooth film covering on the PP subparticles. This change is induced by the extraction with acetone which is a good solvent of the PMMA but not the PP. Keeping this in mind, one could conclude that the grafting polymerization was mainly preceded in the pores of the PP particles. In addition, the PMMA grafting onto the PP chains was the primary polymerization reactions. As expected, this new pathway makes it possible to produce PP-based nano- or submicroscale dispersing multi-component composites which might extend the RGT from the olefins to the vinyl monomers.

Figure 2 shows the FT-IR spectra of PP-g-PMMA samples after extracting with acetone. Compared with the spectrum of pristine PP, strong absorption bands appeared at 1734 cm^{-1} in grafting products. This characteristic band was attributed to the

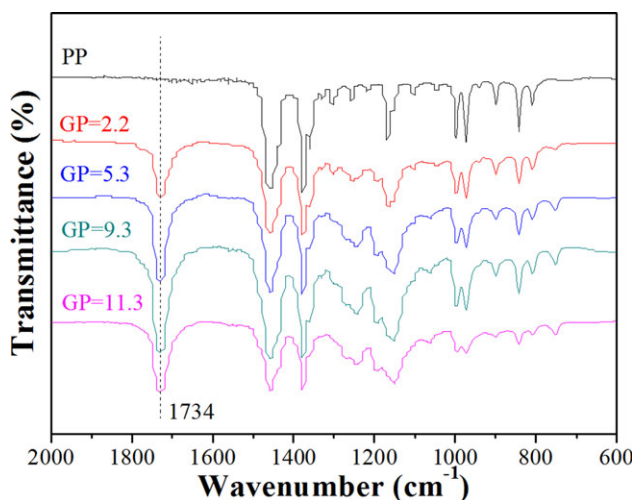


Figure 2. FT-IR spectra of nascent PP and PP-g-PMMA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

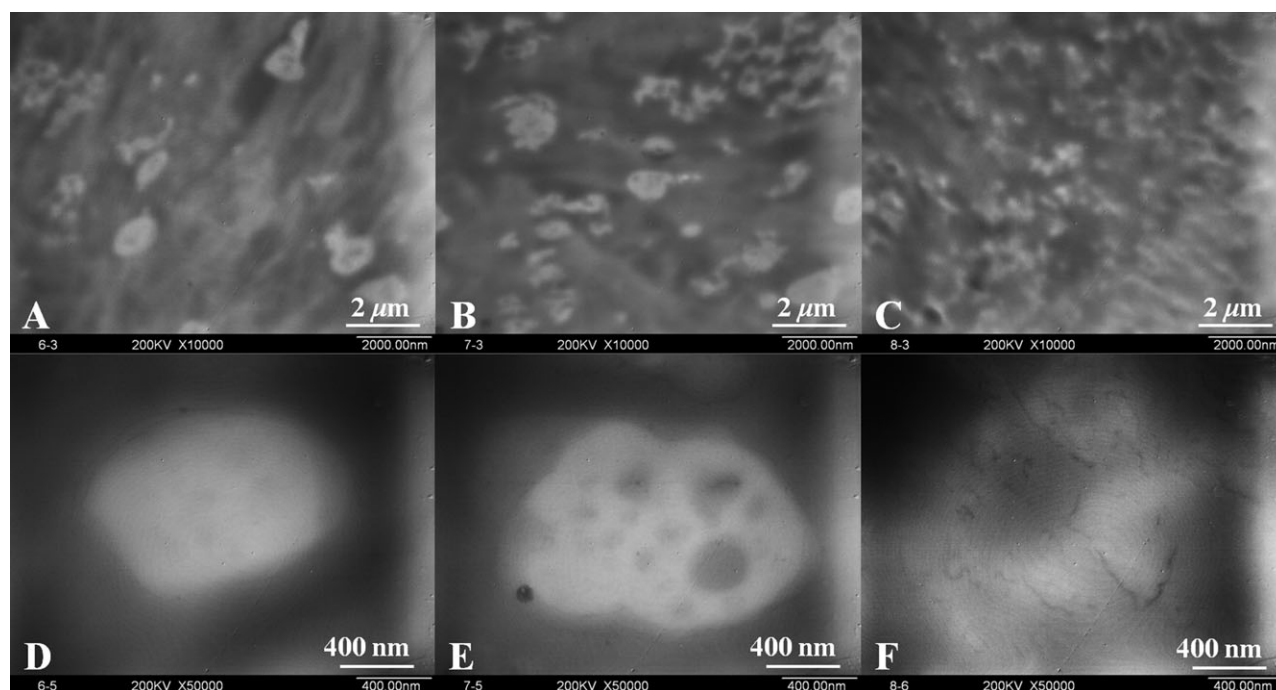


Figure 3. TEM images of PP-g-PMMA after kneading. (A, D) GP = 21.8%. (B, E) GP = 22.7%. (C, F) GP = 25.7%.

stretching of carbonyl group of PMMA. Considering that the homopolymer of PMMA had been removed by the acetone it indicated that the samples were the PP-g-PMMA.

In the industrial field, PP granules are usually used after a melting process. Grafting is a meaningful processing only if a fine dispersion of grafting chains would remain. The microphase structures of PP-g-PMMA samples after kneading in Haake with relatively high GP, from 21.8% to 25.7%, were observed by TEM. As presented in Figure 3(A–C) with the greater magnification of 10^4 , it clearly shows that PP is a dominant phase (the dark region stained by RuO_4) and the PMMA is the dispersed phase with the size of the microdomains less than $1 \mu\text{m}$. With the increase of the GP, the volume fraction of the PMMA phases increases. Interestingly, with the greater magnification of 5×10^4 , it could be observed that some PP microdomains with the size around 100–400 nm are buried in the PMMA microphases in some particular microregions [Figure 3(D–F)]. It could be understood that some PMMA grafting chains interpenetrated among the small PP nuclei and/or fibrils in the grafting polymerization process. When the PP-g-PMMA processed in the molten state, the immiscible PP and PMMA chains formed this complicated finely dispersed microphase structures. As a result of the small size and amount of these PP microdomains, the PP is still a continuous phase in the whole PP-g-PMMA copolymer. In this regard, the solid grafting method presented in this article is a robust process to prepare the PP-based multicomponent polymer blends with the disperse phase domains less than $1 \mu\text{m}$ that cannot be prepared by traditional blending technologies easily.

Main Factors Affecting the GP and GE

The GP and GE are important factors to verify whether graft polymerization is successful. Table I shows the effect of mono-

mer concentration on GP and GE. GP increases from about 2.2% to 13.6% with the increasing MMA feed ratio. However, as GP increases with monomer feed, GE drops from about 78.0% to 61.8%. As is well known, PP is a semicrystalline polymer and grafting polymerization can only occur at amorphous region or micropore surface. The sites suitable for initiating graft polymerization are limited. When the ratio of MMA increased to a critical value, the homopolymerizations of MMA initiated by dissociative radicals would become considerable and resulted in the decrease of GE. However, the minimum of GE is about 61.8%, which implied that the homopolymerizations were extremely prevented in WSGP system compared with the solid grafting.

For solid grafting polymerization, a higher swelling ratio of PP by monomer is helpful to improve the grafting efficiency. It was reported that the sorption of styrene in PP is about 40% compared with 10.3% of MMA.²⁹ So it is safe to say the maximum GP of styrene could be greater than that of the MMA. To further investigate the graft polymerization behavior, styrene was applied as an interfacial agent to swell the PP. As expected the addition of styrene could improve the GP and GE (Compared Run 5 and 6 to the Run 7 in Table I). Xie and co workers³² discussed the effects of the addition of styrene on the melt graft copolymerization of PP with pentaerythritol triacrylate. They claimed that stable styryl radical formed by styrene reacting with PP macroradicals was the key to suppress the β -scission degradation, which contributed to the improvement of the grafting degree. Because the reactivity ratios of MMA–St are $r_{\text{MMA}} = 0.46$ and $r_{\text{St}} = 0.52$, respectively, their azeotropic point is determined to be 0.471.³³ In our experiment, the content of MMA was much higher than 0.471. Therefore, PMMA should be the major component in graft copolymer chain. In this

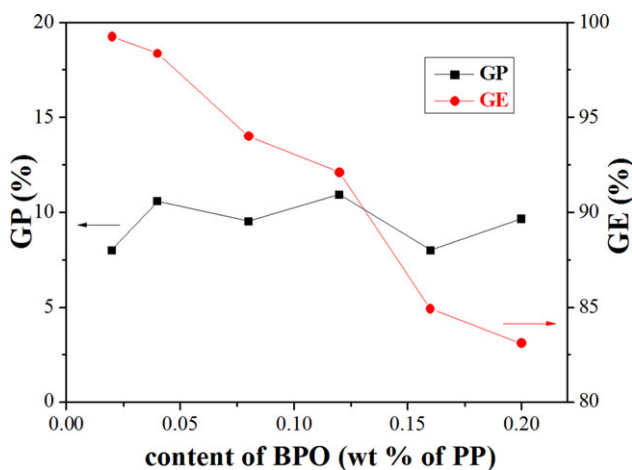


Figure 4. Effect of BPO concentration on GP and GE. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

respect, it could be inferred that the swelling effects of styrene and its reaction with PP macroradical did contribute to the improvement of the GP. However, when the monomer feed was too high both GP and GE dropped, and a great amount of homopolymers formed were found in the reaction medium.

To understand the effect of initiator concentration on the grafting polymerization, the ratios of BPO/PP from about 0.2 to 2.0 wt % were run. As showed in Figure 4, the GP has no significant changes with the increasing BPO usage. However, the GE decreases from about 99.3% to 83.1% with the increasing BPO ratios. Fu and coworkers²⁴ investigated the reaction parameters affecting the gelation and mechanism of graft copolymerization of poly(propylene-*co*-ethylene) granules with styrene. Their results showed that higher initiator and monomer feed led to the higher grafting degree and high content gelation. When the BPO/PP ratio is less than 1% there was no gel formed. That is to say lower initiator concentration is beneficial to the grafting reactions. Our result is consistent with the observations of theirs.

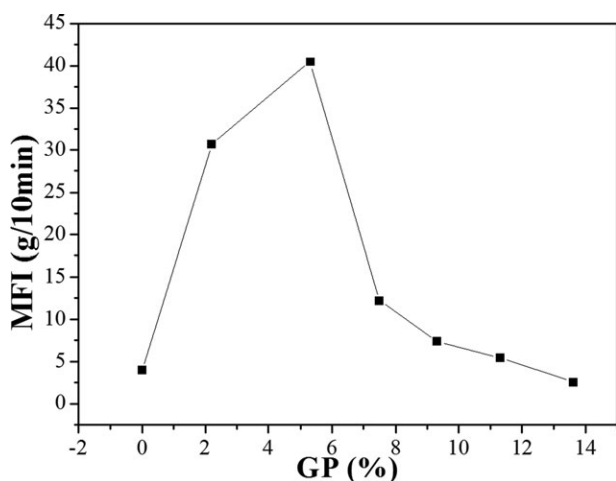


Figure 5. Effect of GP on MFI, 230°C, 2.16 kg.

The Properties of PP-g-PMMA

Effect of GP on the MFI of PP. In the grafting process there are, at least, two competitive reactions related to the PP chain macroradicals. One is the β -scission, which leads the PP chain degradation. The other one is initiating monomers polymerization to form grafting chains. The degradation might result in the reduction of molecular weight or simply the drop of the melting flow index. The effect of grafting chains on MFI is complicated. Many factors, such as the length of grafting chain, grafting density, miscibility of the grafting chains and PP backbone, might have an influence on the MFI of the grafting polymers. Figure 5 shows the relationship of MFI with GP. When the GP is less than 5.3%, MFI increases with the increasing GP. Then MFI drops and closes to that of pristine PP. Generally the PMMA and PP are immiscible, and the interaction among the PMMA/PMMA chains is stronger than that of the PP chains. With a low GP the grafting chain length is short and grafting density is low. In this case PMMA chain is possibly as a plasticizer and enhances melting flow of the polymers. As mentioned above, PP chain degradation taking place in grafting process is not the main reaction of the chain macroradicals, therefore its impact on MFI might be minimized. With the increasing GP, both the length of grafting chains and grafting density are increased. The strong interaction and the entanglement among PMMA chains might result in the drop of the MFI. In fact, it should be kept in mind the influencing factors of MFI in this system is complicated. The high viscosity of the PMMA melt is also possibly contributed to the drop of MFI and more attempts will be necessary to address it in future.

Effect of GP on the Crystallinity of PP. The melting enthalpy (ΔH_m) and melting temperature (T_m) of some typical PP-g-PMMA samples are also listed in Table I. The relative crystallinity (Rc) is calculated by the ΔH_m of PP-g-PMMA divided by 209 J·g⁻¹ for a 100% crystalline PP.^{34,35} Figure 6 shows the effect of GP on Rc and T_m . It was found that the introduction of PMMA grafting chains can disturb the regularities structure of PP. Thus the grafting chains sterically hinder the crystallization of PP that is evidenced by the decrease of the relative crystallinity. In addition, the melting temperature also reduces from

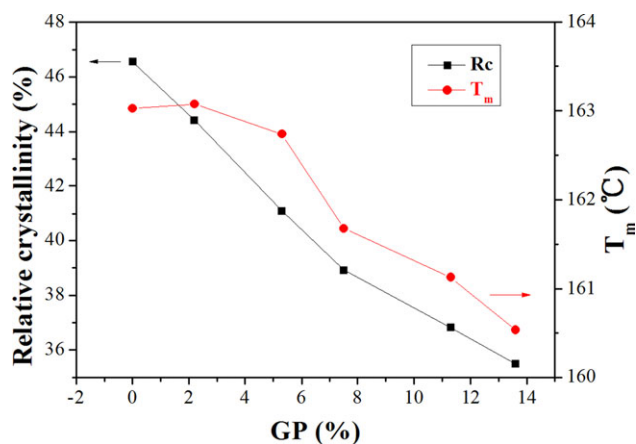


Figure 6. Effect of GP on relative crystallinity and T_m . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

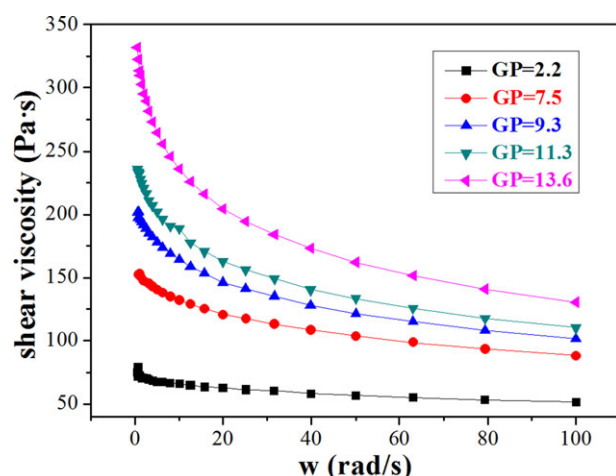


Figure 7. Effect of frequency range on shear viscosity. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

about 164°C to 160°C as the GP increases from about 2.2% to 13.6%. In general, T_m of crystal region is much higher than that of amorphous region. Therefore, PP-g-PMMA with a higher GP has a lower melting temperature, and the changes of melting temperature are comparable to the literatures.³⁴

Rheological Properties of PP-g-PMMA. Shear viscosities (η^+) measured with the rheometer at a temperatures of 200°C are shown in Figure 7. Sharp viscosity drops are found in each curve with increasing frequency, and the shear viscosity of high GP is always greater than that of low GP at given frequency. Moreover, the shear viscosity of low GP is insensitive to the increment of the frequency. However, a small change of frequency would lead to an obvious change of shear viscosity in the case of high GP. These results suggest that grafted-PMMA in PP-g-PMMA enhanced the shear viscosity especially in the case of low frequency. Branched chain structure is more prone to molecular entanglement, and which leads to a higher shear viscosity. At dynamic states, the molecular chains prefer unwrapping and sliding, tending to a more significant reduction in shear viscosity, and showing stronger frequency dependence.

PP-g-PMMA as Compatilizer in PP/ASA Blend. The high shrinkage rate, low melting strength and low impact strength, especially at low temperature, limit the application of PP resin. Therefore, enhancing the toughness of the PP resin is of importance to both the academic and industrial fields. Commercially, the elastomeric polymers, such as ethylene propylene diene monomer, butyl rubber, polyolefin elastomer, and polystyrene-polybutadiene-polystyrene are applied in PP toughing. Although these polymers could improve the toughness of PP, they also

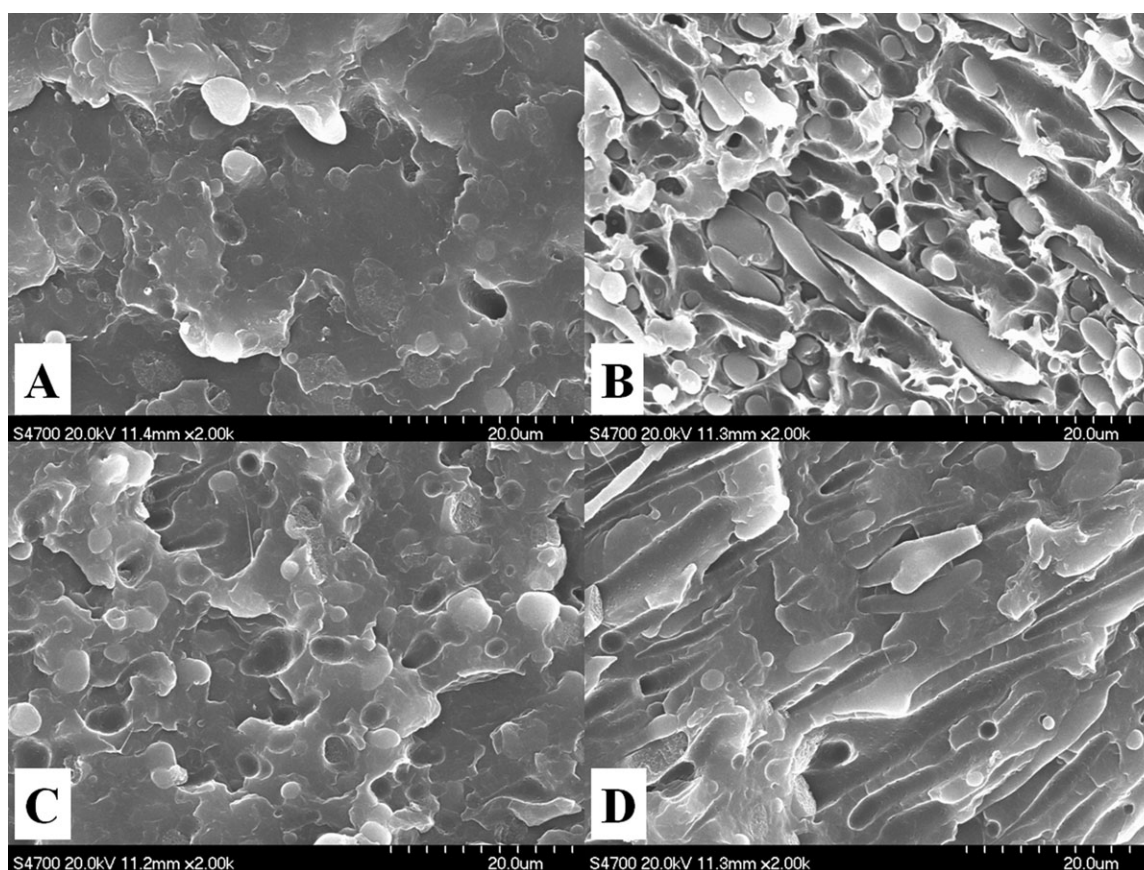


Figure 8. SEM micrographs of PP/ASA blends with PP-g-PMMA (GP = 11.3%) as compatilizer. (A) PP/PP-g-PMMA/ASA = 7/0/3. (B) PP/PP-g-PMMA/ASA = 6/1/3. (C) PP/PP-g-PMMA/ASA = 5/2/3. (D) PP/PP-g-PMMA/ASA = 4/3/3.

resulted in a loss of some properties, such as tensile strength, heat deformation temperature, etc. How to balance these properties is still a challenge. ASA resins have some unique properties, such as weather resistance, high mechanical strength, chemical resistance, thermal stability, antistatic property, and color stability. However, ASA is immiscible with PP and compatilizer is needed when they are blended. Here the PP-g-PMMA was explored as a compatilizer in the PP/ASA composite. Figure 8 shows the morphology of the PP/PP-g-PMMA/ASA composite. As shown in Figure 8(A), there is clearly two microphases, and the rod-like phase of ASA resin is completely peeling off from the PP matrix. It indicates that there is almost no interfacial interaction between the PP matrix and ASA. With the increasing PP-g-PMMA content in the composites, the boundary of microphase becomes not so clear [comparing Figure 8(A, B, and C)]. Furthermore it seems the interfacial interaction is significantly improved. This preliminary result shows the grafting polymer, PP-g-PMMA, is potentially an effective compatilizer in the PP/ASA composite.

CONCLUSIONS

With the porous PP spheres prepared by RGT as the precursor, the PP-g-PMMA was synthesized by WSGP. The GP could be as high as 13.6% with the MMA alone as monomer and with the addition of the styrene as the comonomer the GP went up to 24.5%. Various GPs led to different properties of polymer, such as MFI, relative crystallinity, melting temperature, and shear viscosity. This provides a way to control PP performances by varying reaction conditions, such as BPO and monomers concentration, to control the GP. The PMMA domains could be finely dispersed in PP and controlled less than 1 μm in diameter that cannot be produced by traditional blending easily. Finally, PP-g-PMMA was fully capable of performing the role as compatilizer for PP/ASA blends.

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