

Enhancement of Graft Yield and Control of Degradation During Polypropylene Maleation in the Presence of Polyfunctional Monomer

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ABSTRACT: Free-radical initiated grafting of maleic anhydride (MAH)/polyfunctional acrylate (PFA) multimonomer system onto polypropylene (PP) via reactive extrusion was studied. The effects of PFA and initiator concentration on the grafting reaction were investigated. It was shown that PFA as a comonomer could greatly enhance MAH grafting degree, which increased monotonically as the molar ratio of PFA to MAH increased. The rheology test demonstrated that the viscosity of grafted PP was also promoted as more PFA was used. The formation of branched structure during the grafting process was proved by oscillatory shear rheological analysis. The mechanism

of grafting in the presence of PFA was discussed, suggesting PFA had higher reactivity with PP macroradicals than MAH and therefore forming stabilized macroradicals, thus resulting in depression of β -scission and favoring the formation of branched structure. Higher initiator concentration gave higher MAH grafting degree but more severe degradation. The mechanical properties of the grafted PP were comparable with those of unmodified PP. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 2512–2517, 2011

Key words: maleic anhydride; polypropylene; reactive extrusion; polyfunctional acrylate

INTRODUCTION

The functionalization of polypropylene (PP) through grafting unsaturated polar monomer such as maleic anhydride (MAH), acrylic acid and its derivatives by peroxide initiated reactive extrusion has been a routine way to improve their adhesion and compatibilizing properties.¹ MAH was most often used due to its highly active anhydride group and difficulty in homopolymerization in the free-radical grafting. However, grafting of MAH onto PP in the melt has remained somewhat challenging due to predominance of β -scission caused by the initially formed radicals.² The grafted MAH reached significant level at the expense of greatly reduced viscosity, which was undesirable in some application and the graft-

ing efficiency was often found very low in spite of high concentration of initiator used.³ This was partly explained by the low free-radical reactivity of MAH due to its orbital symmetry and low solubility of MAH in the PP melt. The mechanism of grafting MAH onto PP has been studied and it revealed how grafting reaction and β -scission proceeded, suggesting that the key to enhance the graft yield of MAH and suppress the degradation was to stabilize the macroradicals formed through hydrogen abstraction.⁴

Various methods has been attempted to mediate the MAH grafting process of PP. It was established that styrene as a comonomer could improve the MAH reactivity by reaction with MAH to form styrene-MAH copolymer before the two monomers grafted onto the PP backbone and control the chain scission at a large extent.⁵ However, styrene is not an ideal choice in reaction extrusion due to its high volatility and toxicity. Recently, it was reported that by using a rare earth oxide, neodymium oxide (Nd₂O₃) as a coagent, the grafting degree of MAH can be increased nearly 20%, and melt flow rate (MFI) was also increased at the same time.⁶ By controlled release of primary radicals from organically modified montmorillonite interlayers, nano-reactor concept was also used in the grafting process to result almost double grafting degree at best and less

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TABLE I
Twin-Screw Extruder Configuration

Zone-1	Zone-2	Zone-3	Zones-4-8	Zone-9	Zone-10
36/36T, 2-112/112, 88/88	88/44, 5-56/56, 4-36/36, 2-45°/5/45	36/36, 2-88/88, 88/44	4-56/56, 45°/5/30, 90°/5/30, 88/88, 4-56/56, 90°/5/45	45°/5/, 2-112/112	88/44, 4-56/56

extent of degradation.⁷ Another effective method to control degradation of PP and increase MAH grafting yield was using furan derivatives with a double bond substituted with electron attracting groups as comonomer, which reacted with macroradicals at high addition rate to form stabilized radical.⁸ Similar to furan derivatives, allylic coagent could also reduce β -scission via reaction with PP macroradical, forming stabilized radical.⁹

Polyfunctional acrylate (PFA) was first introduced in reactive extrusion by Wang et al. to prepare long chain branched PP¹⁰ and its application in this field was verified and developed.^{11,12} Al-Malaika et al. has published a series of articles employing PFA as comonomer in the grafting of glycidyl methacrylate (GMA) onto ethylene-propylene rubber,¹³ ethylene-propylene-diene terpolymer,¹⁴ and PP.¹⁵ They found that the presence of PFA gave rise to greatly increased grafting yield and highly depressed homopolymerization of GMA, which could be attributed to higher reactivity of PFA to macroradicals. It was also found PFA could increase MAH grafting degree in the maleation of high density polyethylene (HDPE) accompanied with a modest increase of gel.¹⁶ However, to our knowledge, there is still no public report on PFA application in the maleation of PP. In this article, we investigated how PFA influenced grafting of MAH on PP during the reactive extrusion process and the rheology and mechanical properties of the grafted PP were also evaluated.

EXPERIMENTAL SECTION

Materials

Isotactic PP, F401, was supplied by CNPC Lanzhou Chemical Company. The trimethylol propane triacrylate (TMPTA) was obtained from Tianjin Tianjiao Chemical Company. The free-radical initiator 2,5-dimethyl-2,5-di(tert-butyl peroxy)hexane (DHBP) was supplied by Akzo Nobel Company. MAH was from Sigma-Aldrich. All the materials were used as received.

Melt grafting

The PP pellets, monomer(s), and initiator were blended simultaneously in the high speed mixer before charged into the extruder. The melt-grafting

reactions were carried out in a TSE-30A intermeshing co-rotating twin screw extruder with a 40 : 1 length-to-diameter ratio (10 barrel zones), which was equipped with a loss-in-weight solids feeder. The screw rotating speed was 150 rpm which corresponded to the residence time of about 1 min. The temperature was set to 170°C for the first zone (the feed port) and 200°C for the other zones. Extrudates were cooled in water and then pelletized and dried. The intermeshing, co-rotating screw configuration used was listed in Table I.

Purification and characterization of grafted PP

The grafted PP was dissolved in refluxing xylene at a concentration of 1% (wt/vol), and excess acetone was added to precipitate them. The precipitated samples were filtered, washed, and dried under vacuum at 60°C for 24 h.

The samples thus obtained were then hot-pressed under 190°C under vacuum into thin films and analyzed by fourier transform infrared spectroscopy (FTIR). FTIR spectra were recorded on a Nicolet FTIR-6700.

The grafting degree was also measured through chemical titration method. About 0.5 g purified grafted PP was dissolved in 80 mL of refluxing xylene in a flask, then excessive 0.05N KOH-methanol standard solution was added to the cooled xylene solution, after that, the xylene solution was refluxed again for 30 min, finally the hot refluxed solution was titrated by 0.05N HCL-isopropylol standard solution with phenolphthalein as indicator. The grafted degree was calculated according to the following equation:

$$\text{Grafted maleic anhydride content (wt\%)} \\ = 0.05(V_1 - V_2)/2 \times 980.06/m \times 100\%$$

where V_1 (L) and V_2 (L) were the volume of KOH-methanol standard solution and HCL-isopropylol standard solution, respectively. The weight of the purified PP was represented as m . A total of 0.05 was the concentration (mol/L) of the two standard solutions, and 98.06 represented molecular weight of MAH.

MFI measurements of the samples were carried out using the MFI equipment (Haake SWO 556-0031) at 230°C with a load of 2.16 kg weight according to the ASTM D1238-86T standard.

TABLE II
Effect of Initiator Concentration on Grafting Degree and MFI

	D1	D2	D3	D4	D5
PP (kg)	2	2	2	2	2
DHBP (mol)	0	0.00086	0.00172	0.00258	0.00344
MAH (g)	30	30	30	30	30
Grafting degree	–	0.11%	0.10%	0.12%	0.25%
MFI (g/10 min)	4.8	12.2	18.1	26.7	37.4

Oscillatory shear rheological analysis was carried out with a TA AR-2000 rheometer with a parallel-plate fixture (diameter = 25 mm). The frequency range was 0.02–100 rad/s, and the temperature was 190°C. The strain was kept under 3% to ensure linear viscoelasticity. The measurements were conducted under a dry nitrogen environment to prevent degradation.

An Instron (3365) tensometer was used to test the mechanical properties. The specimens were injection molded. The tensile, flexural, and impact properties were tested according to ASTM D 638, D790, and D256, respectively.

RESULT AND DISCUSSION

Effect of initiator concentration on grafting degree and MFI of grafted PP

Table II listed the formulation of PP, MAH, and initiator in the absence of TMPTA, and the results of grafting degree and MFI were also included. The initiator concentration was varied, whereas the PP and MAH amount were kept at a fixed level. It was shown that grafting degree was very low and exhibited weak dependence on initiator concentration until it reached a relatively high level. At the same time, MFI increased significantly as initiator concentration was raised. This suggested that degradation predominated in the high temperature grafting extrusion process of PP, as more radicals generated by initiator was prone to resulting in severer β -scission, as literatures documented.^{2,5} The FTIR spectra of the virgin PP and PP-g-MAH were shown in Figure 1. When compared with virgin PP, new absorption band at 1784 cm^{-1} was observed in PP-g-MAH. It was demonstrated that single succinic anhydride grafted on chain end should give the symmetric stretching of the carbonyl groups ($-\text{C}=\text{O}$) at 1792 cm^{-1} , whereas 1784 cm^{-1} was assigned to interacting anhydride such as closely grafted, clustered or homopolymerized anhydride.¹⁷ As β -scission would occur after MAH attached to the tertiary carbons,¹⁸ it was difficult to determine the exact location of MAH along PP backbone. However, multiple MAH grafts in close proximity could be generated if intramolecular H-transfer occurred

for MAH,¹⁹ which might be the case for DHBP as initiator. The absorptions at 2723 cm^{-1} could be assigned to the characteristic absorption of the PP skeleton, which was chosen as an internal reference in this case. Therefore, the FTIR result confirmed the grafting of MAH onto PP.

FTIR analysis of grafted PP in the presence of TMPTA

The FTIR spectra of the pure PP, PP-g-MAH, and PP-g-(TMPTA-MAH) were also shown in Figure 1. When compared with PP-g-MAH, new absorption bands at 1738 and 1862 cm^{-1} were observed. The two absorption bands could be assigned to the absorption of the symmetric stretching of carbonyl groups ($-\text{C}=\text{O}$) of TMPTA and unsymmetric stretching of carbonyl groups of MAH, respectively.

The spectra showed that the introduction of TMPTA could significantly increase the grafting degree of MAH. The intensity of the carbonyl absorption band at 1784 cm^{-1} of PP-g-(MAH-TMPTA) obtained from the PP/MAH/TMPTA/DHBP melt grafting system was much stronger than that of PP-g-MAH obtained from the PP/MAH/DHBP system. As used in Ref. 5, the absorbance ratio (Ra) of the areas of the bands at 1784 and 2723 cm^{-1} was calculated to represent the relative grafting degree of MAH.

Effect of TMPTA concentration on grafting degree and viscosity of grafted PP

Figure 2 showed the effect of TMPTA concentration on the grafting degree of MAH and the MFI of the grafted PP, whereas the MAH and DHBP

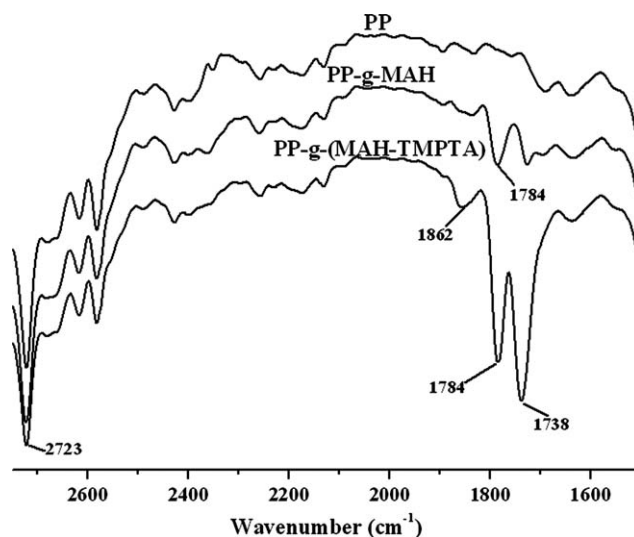


Figure 1 FTIR of PP, PP-g-MAH, and PP-g-MAH-TMPTA.

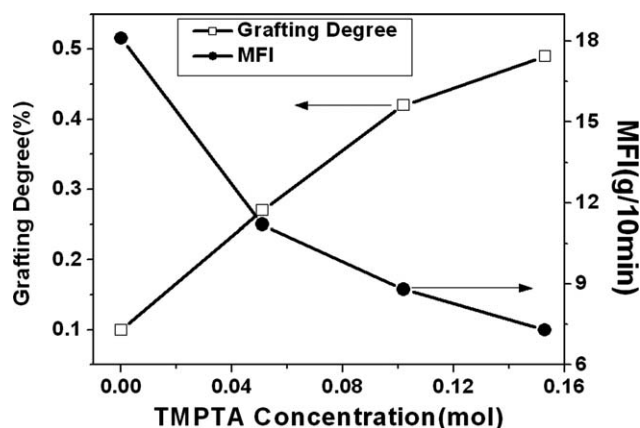


Figure 2 Effect of TMPTA concentration on the MFI and the grafting degree of MAH.

concentrations were kept fixed. The MAH grafting degree of the modified PP was drastically higher in the presence of TMPTA, which was consistent with FTIR result, as showed in Figure 3 and Table III. The Ra values calculated from FTIR were not exactly in accurate accordance with the titration results, which could be explained by the influence of adjacent ester band to the exact calculus of anhydride adsorption band in calculation of areas. However, this little discrepancy could not undermine the conclusion that the grafting degree of MAH increased with the rise of TMPTA concentration.

The MAH grafting degree initially was enhanced greatly when small amount of TMPTA was used, and then increased gradually as TMPTA concentration exceeded 0.10 mol. This suggested more TMPTA would involved in competitive reactions such as branching or grafting when the amount of TMPTA exceeded the level that the copolymerization of MAH and TMPTA needed.

The MFI value of the grafted PP decreased with TMPTA concentration increasing, which meant that

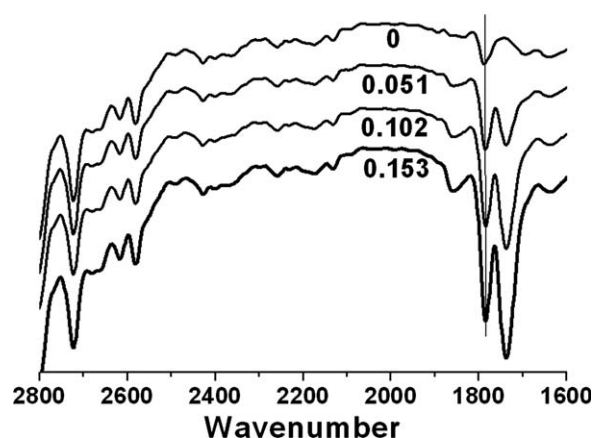


Figure 3 FTIR evidence of TMPTA effect on the MAH grafting degree.

TABLE III
Effect of TMPTA Concentration on Grafting Degree and MFI

	D6	D7	D8	D9
PP (kg)	2	2	2	2
DHBP (mol)	0.00172	0.00172	0.00172	0.00172
TMPTA (mol)	0	0.051	0.102	0.153
MAH (g)	30	30	30	30
Grafting degree	0.10%	0.27%	0.42%	0.49%
Ra	0.31	0.64	1.05	1.23
MFI (g/10 min)	18.1	11.2	8.8	7.3

the addition of TMPTA effectively reduced the degradation of PP. The complex viscosity of virgin PP and grafted PPs were illustrated in Figure 4. When compared with virgin PP, all the grafted PPs exhibited lower viscosity. However, the viscosity was augmented as TMPTA concentration increased, and at the same time, shear thinning occurred at lower frequency and the plateau zone at low shear rate was even completely disappeared for sample D9, which was characteristic of branching structure.²⁰

Mechanism of polyfunctional acrylate-assisted free-radical grafting of MAH onto PP

In styrene assisted MAH grafting onto PP, a complex radical alternating copolymerization mechanism was proposed.⁵ However, unlike styrene, PFA was classified as electron-acceptor monomer, which made it unreasonable for formation of charge transfer complex.²¹ Furan derivative as coagent was used in PP functionalization with MAH to control degradation due to its higher reactivity towards macroradicals with respect to MAH.²² Similarly, in PFA-assisted GMA grafting onto ethylene-propylene copolymer, the presence of PFA could achieve optimum GMA grafting yield at much lower peroxide concentration by almost an order of magnitude,

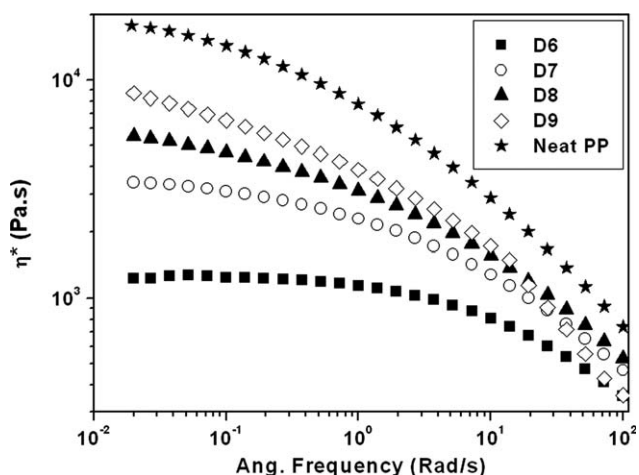


Figure 4 Complex viscosity of grafted PPs.

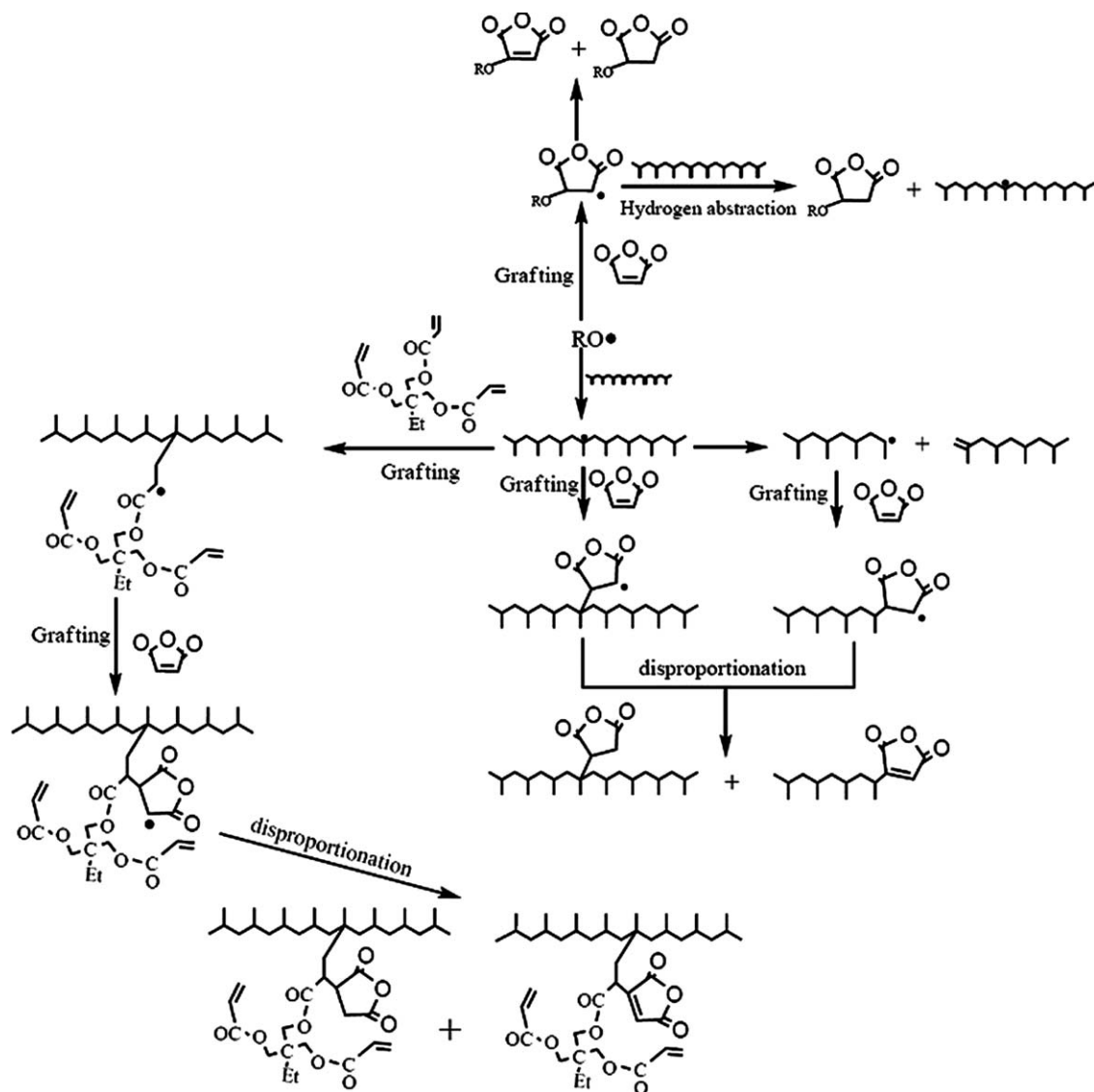


Figure 5 Illustration of grafting mechanism in the presence of TMPTA.

which was attributed to high reactivity of PFA to macroradicals and GMA.¹³ The high reactivity of PFA was also partly supported by high grafting efficiency of trimethylol propane trimethacrylate onto PP.²² The high reactivity of PFA in assisting MAH grafting onto PP was verified by the greatly enhanced grafting yield of MAH in the presence of PFA, which meant PFA reacted with macroradicals before MAH to form stabilized radicals first, then copolymerized with MAH to form PP-g-TMPTA-MAH, as illustrated by Figure 5. Furthermore, when compared with styrene, an obvious advantage of adopting PFA as coagent was the ester polar groups in PFA could provide additional polarity as the target of grafting polyolefin was to improve their polarity.

In the reactive extrusion process of PP/MAH/TMPTA/DHBP system, competitive reaction included β -scission of PP backbone, branching, PFA

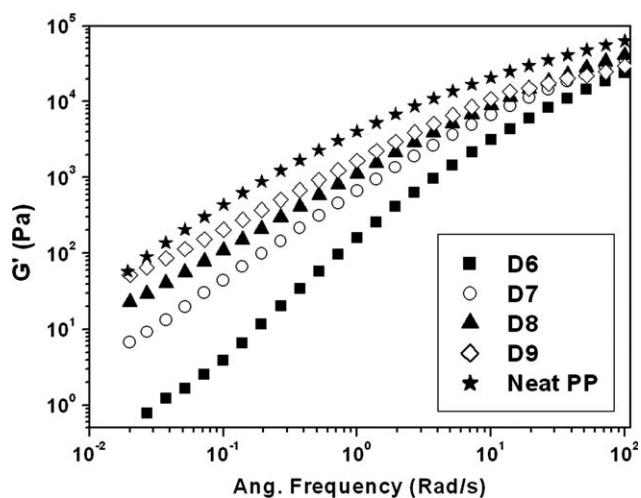


Figure 6 Storage modulus of grafted PPs.

TABLE IV
Mechanical Properties of Grafted PP

Sample	Flexural strength (MPa)	Flexural modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)	Notched izod impact strength (kJ/m ²)
PP	42.5 ± 0.3	1.12 ± 0.04	35.9 ± 0.1	497 ± 55	3.64 ± 0.42
D6	48.6 ± 0.5	1.21 ± 0.06	34.5 ± 0.3	518 ± 78	2.88 ± 0.34
D7	49.7 ± 0.2	1.23 ± 0.05	36.4 ± 0.4	439 ± 37	3.20 ± 0.45
D8	50.4 ± 0.6	1.25 ± 0.04	36.3 ± 0.3	453 ± 63	3.52 ± 0.37
D9	50.7 ± 0.3	1.27 ± 0.03	36.9 ± 0.4	447 ± 75	3.67 ± 0.51

grafting, and homopolymerization. PFA can form an insoluble gel if homopolymerization initiated by the alkyl-oxide radicals occurred.¹³ However, we found no gel in the purification of grafted PP via xylene refluxing. This was consistent with the result of Wang et al., who observed macrogels of crosslinked PP and PFA homopolymer were difficult to form if peroxide and PFA concentration were controlled below a certain level.¹⁰ The formation of long branched chain was evidenced by rheological test, as shown in Figures 4 and 6. In addition to higher viscosity and stronger shear thinning at low shear rates, the storage modulus of grafted PPs increased and the slope at low frequency decreased with the ratio of PFA to MAH enlarged, which were believed to be the characteristic of branching structure.²⁰ This indicated more PFA was involved in branching as its concentration increased. The PFA grafting could not be excluded but it was difficult to distinguish from the other reactions.

Mechanical properties of grafted PP

The mechanical properties of MAH grafted PP were rarely reported²³ although they were very important in some applications. We tested the mechanical properties of virgin PP, PP-g-MAH, and PP-g-TMPTA-MAH, and the results were listed in Table IV. It could be concluded that the excellent properties of PP were largely preserved and improved.

CONCLUSIONS

In this work, an effective method to enhance MAH grafting yield onto PP and control degradation at a large extent was reported. The degree of grafting was drastically increased with the introduction of tri-functional acrylate as a coagent and the viscosity elevated simultaneously. This was attributed to the high reactivity of tri-functional acrylate with both the PP macroradicals and MAH, which led to the depression of β -scission during grafting reaction.

The formation of branched PP was also proved according to the dynamic rheology analysis. The mechanical properties of grafted PP were as good as those of the virgin PP.

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