

Physical Properties of PP-g-AA Prepared by Melt Extrusion and its Effects on Mechanical Properties of PP

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ABSTRACT: Polypropylene grafting with acrylic acid, PP-g-AA (FPP), was prepared by melt extrusion. The physical properties of FPP and effect of FPP on mechanical properties of polypropylene (PP) were investigated. Experimental results showed that an increase in the grafting rate of FPP resulted in an increase in the crystallization peak temperature, melt peak temperature, and degree of crystallization of PP. Double melting peaks were observed for OPP prepared by adding dicumyl peroxide into PP and FPP with low grafting rate due to the degradation of PP. As the grafting rate was increased, the double melt peaks converted into a single melt peak. It is suggest that FPP with higher grafting rate resulted in enhanced nucleation and crystallization ability of PP. The grafting of AA onto the PP chain improved the thermal stability and mechanical properties of PP materials. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 2609–2616, 2001

Key words: polypropylene; functionalized polypropylene; crystallization behavior; mechanical property; polypropylene grafting with acrylic acid

INTRODUCTION

There have been many reports about polypropylene (PP) grafting with a polar monomer, especially maleic anhydride (MAH),^{1–7} which mentioned the effect of different initiators,¹ grafting temperature,^{2,3} grafting time,⁴ solvent,^{5,6} and other additives⁸ on grafting reaction, grafting mechanism,^{9–14} structures, and properties of grafting polymer.^{4,5,11,15–20} However, study on PP grafting with acrylic acid (PP-g-AA) is less than that on PP-g-MAH.^{21,22} Zhang et al.²¹ prepared

PP-g-AA by melt extrusion. An increase in the grafting rate and a decrease in the conversion rate were observed with increasing the acrylic acid (AA) concentration. When the dicumyl peroxide (DCP) concentration increases, the grafting rate, conversion rate, and melt flow index (MFI) all increase. Rao²² et al. found that as the grafting rate and acrylic acid homopolymer (PAA) increased, the efficiency of grafting and melt viscosity decreased as the AA concentration was increased during melt grafting. The grafting polymer is a β -crystal nucleating agent for PP crystallization. Grafting AA onto PP resulted in increased crystallization temperature and thermal stability of PP. However, few reports are observed on the effects of PP-g-AA with different grafting rate on structures and properties of PP. In this article, polypropylene grafting with acrylic acid, PP-g-AA (FPP), with different grafting rates was prepared by melt extrusion. Crystallization

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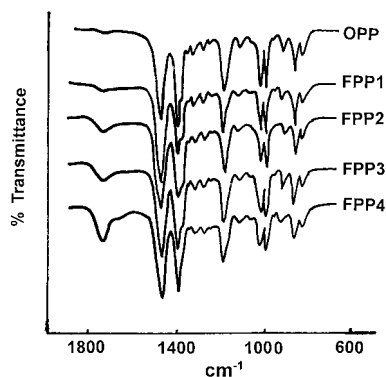


Figure 1 FTIR spectra of OPP and FPP with different grafting rate.

and melting behavior, thermal stability, crystal form and crystalline morphology of FPP, and the effects of FPP on mechanical properties of PP were studied.

EXPERIMENTAL

Materials

Polypropylene (PP), powdered F401, was a commercial product of Guangzhou Petrochemical Co., China. Pelletized PP, 1600, was obtained from Beijing Yanshan Petrochemical Co., China. Chemical-grade acrylic acid (AA) was purchased from Fushan Chemical Factory, Guangdong, China, and used without further purification. Chemical-grade dicumyl peroxide (DCP), used as an initiator for the AA grafting reaction, was a commercial product of Shanghai Chemical reagent Factory, China. The solvent, acetone, was obtained from Guangzhou Chemical reagent Factory, China.

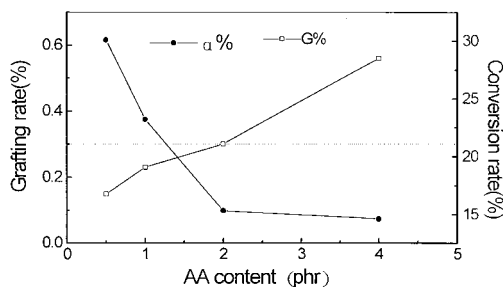


Figure 2 Influence of AA content on grafting rate and conversion rate of FPP.

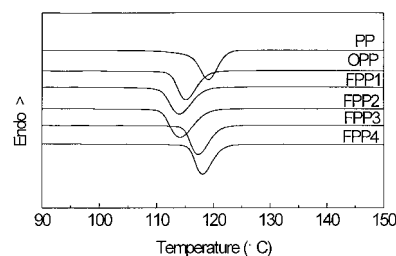


Figure 3 DSC cooling curves of PP, OPP, and FPP.

Preparation of Samples

Preparation of PP-g-AA

DCP and AA were dissolved in acetone, totally blended with powdered PP in a GH-10 high-speed mixing machine. After the solvent, acetone, had completely evaporated, the mixture of AA and DCP was coated on the surface of the powdered PP, and the pretreated PP was prepared. The pretreated PP was then extruded by a SHJ-53 twin-screw extruder at temperatures of 185–190°C, with the screw speed set at 60 rpm. The extruded products, the AA grafting-modified PP (FPP), were frozen in-line in a water bath, dried, and granulated to less than 3 mm.

Preparation of Test Specimens

The mixtures of pelletized PP and the FPP with different grafting rate were dried at a temperature of 90°C for 4 h and injection molded into test specimens using a CJ150 ME-NC injection molding machine, set with a barrel temperature profile ranging from 190 to 210°C. The shape and size of the test specimens were described elsewhere.²³

Characterization of Structure and Properties

Mechanical properties were determined in both tension and flexure, and under impact loading. Tensile properties were measured on a WD-5A

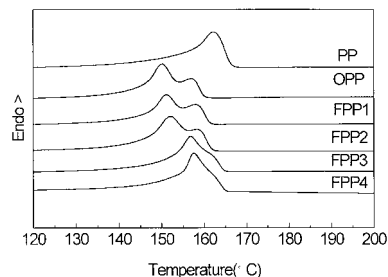


Figure 4 DSC heating curves of PP, OPP, and FPP.

Table I DSC Results of PP, OPP, and FPP

	G (%)	T_{mo} (°C)	T_m (°C)	T_{co} (°C)	T_c (°C)	X_m (%)
PP		155.3	—	162.2	119.1	38.9
OPP	0	145.2	150.1	157.0	115.2	38.5
FPP1	0.15	145.8	152.2	157.6	114.0	39.0
FPP2	0.23	145.6	152.1	158.4	114.1	39.9
FPP3	0.30	151.5	156.8	161.9	117.3	41.7
FPP4	0.56	153.5	157.6	—	118.1	43.1

$$\Delta H_f = 207.15 \text{ J/g.}^{24}$$

electronic universal testing machine (Guangzhou test machine factory, China) at a crosshead speed 10 mm/min, in accordance with GB/T1040-92. Flexural properties were measured on a LWK-5 electronic tension testing machine (Guangzhou test machine factory, China) following GB1040-92 using a crosshead speed of 10 mm/min and a specimen span length of 50 mm. Izod impact strength was performed on a XJJ-5 impact testing machine (Chengde test machine factory, Hebei Province, China) on notched specimens, using procedures given in GB/T1043-93. Reported values were the average of five measurements for each sample at room temperature.

Melting and crystallization of the samples were studied by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC-7 in a nitrogen atmosphere with 10°C/min heating and cooling. The samples were heated from 30 to 220°C, and held at that temperature for 3 min. The nonisothermal crystallization process was recorded from 220 to 50°C, followed by heating from 50 to 210°C for the second heating run. The crystallization and melting parameters were obtained from the cooling and reheating scans. The transition temperature and heat of crystallization and fusion were calibrated using an indium standard.

The WAXD diffractograms were obtained using a Rigaku D/max-III A diffractometer with a tube voltage 35 kV, tube current 25 MA, and CuK α radiation, registered between $2\theta = 5\text{--}35^\circ$.

Some compositions were characterized on a Nicolet 205 FTIR spectrophotometer. Samples were dissolved for 7 h by refluxing of xylene, following by cooling down, then precipitated by acetone three times. The extracted sample was vacuum dried for 19 h in 70°C, and then diluted with KBr powder. The grafting rate was obtained according to the method of ref. 21.

Thermal degradation of the samples were investigated with a Shimadzu TGA-50 thermogravimetric analyzer. Thermogravimetric analysis (TGA) was performed at a heating rate of 20°C/min and a nitrogen flow rate of 33 mL/min. Through the above analyses, the pyrolysis peak temperature (T_{pm}), the temperature of 5 wt % weight loss ($T_{5\%}$), and the weight loss at different temperatures were obtained.

The microscopical observations were performed with a Olympus BH-2 Polarized light microscope. The samples were prepared crystallization for 3 h at 130°C after melting at 210°C for 3 min.

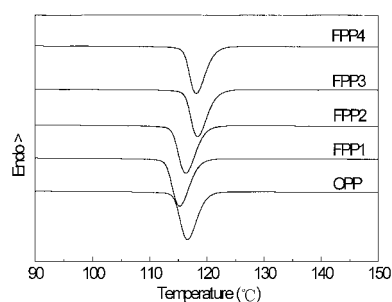
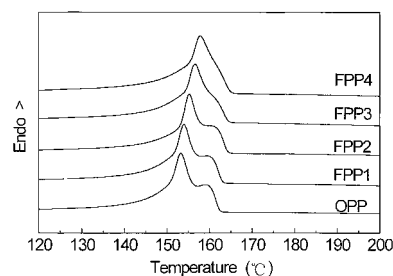
**Figure 5** DSC cooling curves of extracted sample of OPP and FPP.**Figure 6** DSC heating curves of extracted samples of OPP and FPP.

Table II DSC Analysis Data of Extracted FPP

	T_{mo} (°C)	T_m (°C)	T_{co} (°C)	T_c (°C)	X_m (%)
OPP	149.5	153.3	159.6	119.9	39.3
FPP1	150.5	154.1	160.0	119.7	38.4
FPP2	152.2	155.3	161.2	119.7	39.2
FPP3	153.0	156.6	161.3	121.7	38.0
FPP4	153.9	157.9	121.3	118.1	39.8

RESULTS AND DISCUSSION

Effects of the AA Concentration

Many factors have effects on grafting reaction, such as the monomer content, initiator concentration, grafting temperature, time, etc. FTIR spectra of extracted sample are shown in Figure 1, together with the IR observation for the PP. Comparing the spectra for the PP and FPP, a large absorption peak was observed at 1721 cm^{-1} for the functionalized PP, which was attributed to the characteristic absorption of carboxylic group. The intensity of absorption peak at 1721 cm^{-1} increased with increasing the AA concentration. This experimental result indicated that PP was grafted with AA. According to the method of ref. 21, the grafting rate (G%) and conversion rate ($\alpha\%$) calculated from the IR spectra are shown in Figure 2. It can be seen that the G% gradually increases and $\alpha\%$ decreases with increasing the AA content.

Crystallization and Melting Behavior of FPP

Grafting of AA onto PP influenced the crystallization temperature and melting temperature of PP. The DSC curves of nonextracted PP and FPP are shown in Figures 3 and 4. The crystallization and melting parameters are presented in Table I. Compared to PP, a depression in the onset temperature of crystallization (T_{co}) and temperature of crystallization peak (T_c) and a wider shape of the peak of OPP prepared by adding DCP in PP

are observed. A drop in T_{co} and T_c of OPP indicated retardation of the crystallization process and depression of crystallization rate, as evidenced by broadening of the crystallization peak during the DSC cooling scans. The FPP with the lower G% was found to exhibit a lower T_{co} and lower T_c relative to OPP, which were attributed to the suppressed mobility of PP chain in the presence of FPP. However, for the higher G%, the T_{co} and T_c of FPP shifted to high temperature with increasing the G%. When the G% was 0.56%, the T_{co} and T_c of FPP4 were higher than those of OPP and close to the T_c of PP, indicating a higher nucleation ability. It is suggested that the FPP with higher grafting rate accelerated the crystallization of PP due to the effect of enhanced heterogeneous nucleation of PP. It had been reported that the carboxylic group introduced into the PP chain exhibited the effects of the nucleating agent.²² This increased crystallization (and nucleation) rate significantly increases the degree of crystallization of the PP.

For the second heating run, the pure PP sample showed a single melting peak, and the OPP prepared by the addition of DCP in PP exhibited double melting peaks. Compared to the PP, a significant drop in the onset melting temperature (T_{mo}) and temperature of melting peak (T_m) of OPP was observed. The decrease of the T_{mo} and T_m of OPP indicated that the crystal growth was retarded, resulting in a decreased lamellae thickness of PP. It may be attributed to the decrease in the molecular weight and regularity by the scis-

Table III DSC Analysis Data of Nonextracted FPP3 by Multiscans

No. of Scans	T_{mo} (°C)	T_m (°C)	T_{co} (°C)	T_c (°C)	X_m (%)
1	151.5	156.8	161.9	117.3	41.7
2	151.0	156.5	161.6	117.7	41.3
3	150.8	156.7	161.5	117.5	41.0

Table IV TGA Results of PP and FPP

	$T_{5\%}$ (°C)	T_{pm} (°C)	Weight Loss (wt %)			
			300°C	400°C	450°C	500°C
OPP	384.2	472.5	0.5	8.3	37.0	99.9
FPP1	382.8	470.7	0.8	8.4	37.2	99.7
FPP2	393.2	473.6	0.5	6.6	31.1	99.8
FPP3	396.0	476.8	0.6	5.8	26.6	99.5
FPP4	406.9	483.4	1.0	4.6	18.7	99.4

sion and degradation of PP chain and the formation of two kinds of crystals with different lamellae thickness distribution. The FPP was also found to exhibit double melting peaks. However, the T_{mo} and T_m of FPP are higher than those of the OPP sample, and a shift to high temperature with increasing the G% of FPP. When the G% was up to 0.56%, the lower temperature melting peak of FPP4 shifted to high temperature and converted to a single melt peak with a shoulder peak in the higher temperature area of melting peak. The formation of the double melting peak of FPP is mainly related to the degradation of PP. The increase in the T_{mo} and T_m of FPP with increasing the grafting rate indicated that the crystal growth was facilitated, resulting in a larger lamellae thickness and better crystalline perfection of PP in the FPP. It is suggested that the formation of larger amounts of FPP resulted in enhanced heterogeneous nucleation of FPP, leading to the PP crystallization in a higher temperature and the crystallization of a normally noncrystallizing PP chain. Therefore, the FPP with higher grafting rate showed a higher crystalline perfection, melting point, and degree of crystallization. The polar group (—COOH) introduced into PP chain accelerated the nucleation and crystallization of PP. A lot of study had indicated that organic acids, such as adipic acid, could act as nucleating agents for PP. It is believed that the carboxylic group introduced onto the PP chain exhibits enhanced heterogeneous nucleation effect, increased crystallization temperature, degree of crystallization and crystalline perfection of PP.

Figure 5 and 6 are DSC curves of the extracted sample. The crystallization and melting parameters are presented in Table II. It can be seen from Table II that the T_{mo} , T_{co} , and T_c of the extracted sample are higher than that of nonextracted sample. The one reason was that the worst regular

parts of the PP molecular chain were extracted during the extraction, which benefited the crystallization of PP and the formation of crystals with higher melting point. Table III is the result of DSC multiscans of nonextracted FPP3. It was observed that the number of DSC scans had not influenced the crystallization and melting behavior of the FPP.

Thermal Degradation of FPP

The results of thermalgravimetric analysis (TGA) of extracted samples of PP, OPP, and FPP are shown in Table IV. It was found that the temperature of 5 wt % weight loss ($T_{5\%}$) and pyrolysis peak temperature (T_{pm}) increased with increasing the grafting rate of FPP, and that the FPP4 with higher grafting rate exhibited a higher temperature of the pyrolysis peak (T_{pm}). A decrease in the weight loss at 400 and 450°C was also observed. However, the OPP and FPP almost completely decomposed at 500°C. These results indicated that the grafting of AA onto PP chain resulted in the improvement of thermal stability of PP. It is suggested that the improvement of

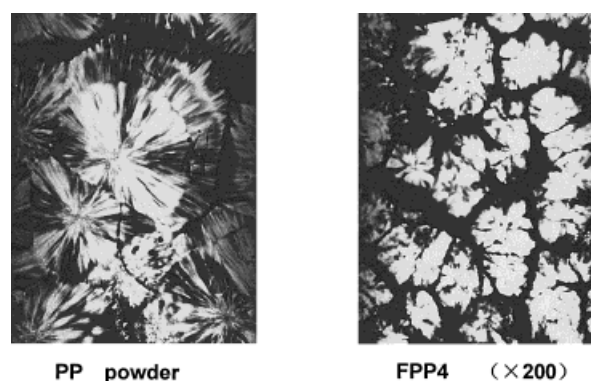


Figure 7 Polarized light microphotographs of PP (a) and FPP4 (b) crystallized at 130°C for 3 h ($\times 130$).

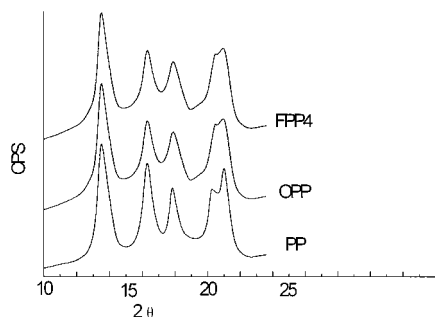


Figure 8 WAXD spectra of PP, OPP, and FPP4.

thermal stability is related to the polarity of FPP. When the polarity of FPP was increased, the effect of hydrogen bonding increased and intermolecular force strengthened, which decreased the activity of H attached to the tertiary carbon in the PP main chain. As a result, the thermal stability was improved.

Crystallization Morphology of FPP

Figure 7 shows the polarized light microphotographs of PP and FPP4 crystallized at 130°C for 3 h. The spherulite of PP with diameter of about 15 μm was observed, and the interface between spherulite was clear. The size of the spherulite of FPP4 became smaller (about 2–4 μm). This result indicated that the density of crystal nucleus of FPP4 was higher than that of neat PP due to the enhanced nucleation effect of FPP4. The smaller spherulite resulted in an increase in the impact property of PP. Observed by WAXD (Fig. 8), PP, OPP, and FPP are all in α -crystal form. Although there are some reports that the β -crystal of PP was formed by grafting AA onto PP, in this article the β -crystal of PP was not observed.

Effect of FPP on Mechanical Properties of PP

The mechanical properties of PP with the addition of 5 wt % FPP are shown in Table V. It was found that the impact, flexural, tensile properties

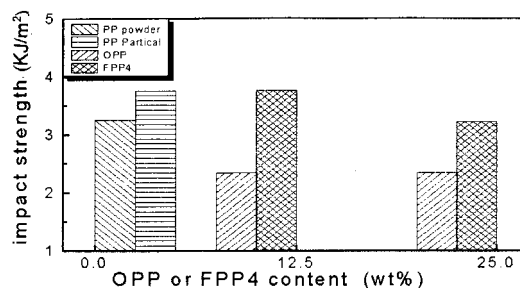


Figure 9 Impact strength of OPP/PP and FPP4/PP.

of powdered PP samples were a little lower than that of pelletized PP. By addition of FPP1 with the lower grafting rate into pelletized PP, the impact property of PP had a little decrease, and flexural strength (FS), tensile property (TS, TM) slightly increased. However, as the grafting rate of FPP was increased, the impact property of FPP/PP increased. The impact property (4.03 kJ/m^2) of FPP4/PP material was even higher than that of pelletized PP (3.76 kJ/m^2). The flexural modulus (FM) also increased. Tensile property was not significantly affected by the grafting rate of FPP. Whether addition of FPP or not, elongation at break were all over 250%. Therefore, it is suggested that the addition of FPP in PP resulted in the improvement of the mechanical properties of PP.

The effects of higher contents of OPP and FPP4 on mechanical properties of PP are shown in Figures 9–11. It can be seen that the mechanical properties of OPP/PP were lower than that of FPP4/PP, especially the impact strength. The impact property of PP was markedly decreased by addition of 12.5 wt % and 25 wt % OPP in PP due to the lower molecular weight and impact strength of the OPP. However, the impact property of PP was not significantly affected by the addition of the FPP4 content of 12.5 wt %, and was higher than that of OPP/PP. Although the impact strength of FPP4/PP decreased with increasing the content of FPP4, FPP4/PP exhibited

Table V Mechanical Properties of PP and FPP/PP

FPP/PP wt %	IS (kJ/m^2)	FS (MPa)	FM (GPa)	TS (MPa)	TM (GPa)	EB %
Powdered PP	3.25	47.8	1.7	29.4	1.4	>250
Pelletized PP	3.76	49.2	1.6	30.9	1.5	>250
FPP1/PP(5/95)	3.57	52.4	1.4	31.2	1.6	>250
FPP4/PP(5/95)	4.03	51.4	1.4	31.9	1.6	>250

a higher impact strength than that of OPP/PP. The similar results were observed for the flexural and tensile strength. The tensile strength of FPP4/PP was higher than that of OPP/PP. The impact, tensile, flexural strengths of FPP4/PP by addition of the FPP4 content of 12.5 wt % were higher than that of pure PP or OPP/PP. It is suggested that the intermolecular interaction by hydrogen bonding of FPP4 improved the mechanical properties of PP. The enhanced nucleation, accelerated crystallization, increased degree of crystallization, and decreased the size of spherulite resulted in an increased the number of interlamellar and interspherulitic ties and the improvement of the impact, flexural, and tensile strength. Therefore, addition of FPP into PP not only increases the polarity of PP matrix, which results in the improvement of the interfacial adhesion between two components of PP composites, but also increases the mechanical properties of materials.

CONCLUSIONS

In this article, polypropylene grafting with acrylic acid, PP-g-AA (FPP), with different grafting rates was prepared by melt extrusion. Crystallization and melting behavior, thermal stability, crystal form and crystalline morphology of FPP, and the effects of FPP on mechanical properties of PP were studied. FTIR experimental results indicated that PP was grafted with AA. The grafting rate gradually increases with increasing the AA content. The onset temperature of crystallization (T_{co}) and temperature of crystallization peak (T_c) of FPP shifted to a high temperature with increasing the G%. It is suggested that the FPP with a higher grafting rate accelerated the crystallization of PP due to the effect of enhanced heterogeneous nucleation of PP. This increased

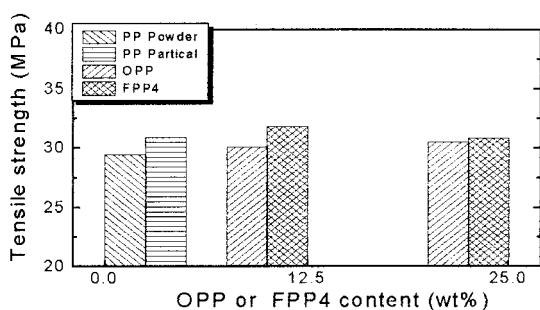


Figure 10 Tensile strength of OPP/PP and FPP4/PP.

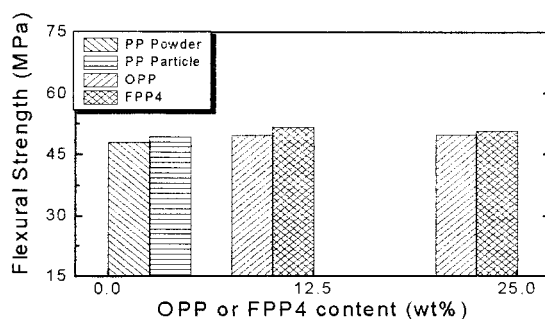


Figure 11 Flexural strength of OPP/PP and FPP4/PP.

crystallization (and nucleation) rate lead to an increased degree of crystallization of the PP. The onset melting temperature (T_{mo}) and temperature of melting peak (T_m) of the FPP was also found to exhibit double melting peaks. However, the T_{mo} and T_m of FPP shifted to a high temperature with increasing the G% of FPP and converted to a single melt peak with a shoulder peak in the higher temperature area of the melting peak. It is suggested that heterogeneous nucleation of FPP resulted in the PP crystallization in a higher temperature and higher crystalline perfection, melting point, and degree of crystallization. The grafting of AA onto PP chain resulted in the improvement of thermal stability of PP. The size of the spherulite became smaller. The β -crystal of PP was not observed. Addition of FPP in PP resulted in the improvement of the mechanical properties of PP.

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