Front. Chem. China 2008, 3(2): 133–137
DOI 10.1007/s11458-008-0025-0

RESEARCH ARTICLE

Chuanlun CAI, Qiang SHI, Lili LI, Ligang YIN, Gongben TANG, Jinghua YIN

Preparation, structure and properties of PP-*g*-AA grafting copolymer

Abstract Polypropylene grafting with AA was prepared by reactive extrusion with pre-irradiated PP (rPP) as the homogeneous initiator. The effects of the pre-irradiated dose, the fraction of rPP and the concentration of acrylic acid on the grafting reaction were studied and the grafted PP was characterized by Fourier transition infrared spectroscopy (FTIR), differential scanning calorimeter (DSC) and polarized light microscopy (PLM). The results show that the degradation of PP was suppressed efficiently with this novel method for preparing PP-*g*-AA copolymers, and the grafted copolymers with good mechanical properties were obtained. It was found that the product with higher graft degree (G_d)(0.19%) and relatively excellent mechanical properties can be produced if the mass ratio of PP/rPP/AA is 90:10:0.8, where the selected pre-irradiation dose of rPP is 4 kGy. Moreover, an adhesive strength of 4.88 kN/m was reached in the PP-*g*-AA/aluminum laminate.

Keywords polypropylene, acrylic acid [AA], reactive extrusion, pre-irradiation

1 Introduction

The pre-irradiation technique is a clean and effective method for modification of polypropylene (PP) and a number of reports on grafting polar monomer onto pre-irradiated PP (rPP) films, fabrics and powders have been published [1–4]. One disadvantage of this technique is that PP is susceptible to degradation induced by irradiation [5], resulting in poor processing properties and poor mechanical properties of the final products. Moreover, the cost of pre-irradiation on large amount of PP restricts the application of modification of PP by this method. Therefore, a major challenge is to devise processing conditions so as to minimize or control the degradation while at the same time maximizing the graft degree to achieve optimal product properties. In this study, the desired amount of macromolecular peroxide was produced on the chains of PP by pre-irradiation and this kind of PP (rPP) was used as ‘‘initiator’’ to initiate the grafting reactions by reactive extrusion with the acrylic acid (AA) as the monomer. The degradation of PP was suppressed efficiently with this novel method for preparing PP-*g*-AA copolymers and the grafted copolymers with good mechanical properties were obtained.

Translated from *Chinese Journal of Applied Chemistry*, 2007, 24(7): 737–741 [译自: 应用化学]

Chuanlun CAI, Qiang SHI, Lili LI, Ligang YIN, Gongben TANG, Jinghua YIN (✉)
State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China
E-mail: yinjh@ciac.jl.cn

2 Experimental

2.1 Reagents and apparatus

Powder PP with a melt flow rate (MFR) of 3.3 g/10 min (2.16 kg, 230°C) was the commercial product obtained from Panjin Ethylene Plant, Chin. Acrylic acid (AA) (AR reagent) was supplied by the Tian Jin Institute of Chemical Reagents (China) and used without any further purification. Xylene, acetone and other reagents were commercial products and used as received.

For the FTIR analysis, approximately 100 μm thickness films were prepared by hot pressing the purified samples. FTIR spectra were obtained on a FTS-135 IR spectrophotometer (Bio-rad Company, US). All the spectra were recorded at a resolution of 4 cm^{-1} with the accumulation of 32 scans.

Differential scanning calorimetry (DSC) was conducted with Perkin- Elmer Diamond differential scanning calorimeter (Pyris software) with samples of 6–7 mg at standard heating or cooling rate of 10°C/min, under nitrogen. The scanning temperatures are in the range from 50 to 200°C.

The polymorph was observed by a polarized-light optical microscope (Leica, Germany) with a hot-stage (Linkam TM600). The sample was crystallized isothermally at 130°C. The MFR of PP-*g*-MAH samples was measured with a XRZ400 MFR tester (China), according to ASTM D 1238.

The mechanical properties of the samples were determined through static tensile and impact-resistant tests according to GB/T 1040–92(China) and GB/T 1043–96, respectively. The standard samples for measurement were molded by injection and annealed for at least 24 h before the tests. 180° Peel strength analyses of modified PP on aluminum substrate was used to determine the adhesive property of grafted products. The measurements were performed on Instron 1121 machine (UK) with a crosshead speed of 50 mm/min (GB/T2790–95). Five measurements were carried out for the average of the results.

2.2 Pre-irradiation

The powder PP was placed in a special container with about 1 cm thickness and irradiated by an electron accelerator (RDI Dynamitron, US) with a limited power of 60 kW and a current of 40 mA. The irradiation was carried out in the presence of air at room temperature. The radiation dose was 4 kGy with a dose rate of ca. 1.1 kGy/s. Hereafter, the commercial product of PP and the PP irradiated by the electron beam are referred to as PP and rPP, respectively.

2.3 Graft copolymerization and purification

The graft reaction of PP with AA was carried out in a home-made co-rotating twin-screw extruder. The diameter of the screw is 30 mm and the ratio of length to diameter (L/D) is 44. The L/D of the reactive zone is 24 and 16 for the melting zone. The maximum torque is 2 × 147 N·M. The barrel of the extruder is divided into 11 segments and each segment is heated independently. The fluctuation of the processing temperature is within ± 5°C. The rotating rates of the feeder screw and the main screw were 19 and 10 rpm, respectively. Under these conditions, the residence time is about 2 min. The temperature of the feeding zone, the mixing zone, the reacting zone and the exit die were 175, 190, 200 and 190°C, respectively. PP/rPP/AA was premixed at a definite ratio before adding into the hopper of extruder, and the ungrafted AA monomer was removed by vacuum. The components of materials were listed in Table 1. The grafting AA onto thoroughly irradiated PP was followed the same procedure.

The grafted samples were purified by solubilization-precipitation procedure. About 2 g of raw grafted sample was dissolved in 100 mL of boiling xylene, and then the solution was poured in 400 mL acetone with stirring to precipitate the grafted PP. The precipitate was filtered by vacuum and washed with acetone for five times. The procedure was repeated twice in order to eliminate the residual completely. The purified samples were dried in vacuum at 60°C before characterization.

3 Result and discussion

3.1 The formation of PP-*g*-AA

The FTIR spectra of neat PP and purified grafted PP are shown in Fig. 1. The characteristic absorption band for the carboxylic group(>C=O) stretching appeared at 1710 cm^{-1} for the acrylic acid grafted PP, indicating that the grafting reaction has occurred. It was also found that the peak height at 1710 cm^{-1} varied with the different samples. The calibration equation reported in our previous work [6] was used for the quantitative measurement of grafting degree (G_d).

$$G_d = 9.468 \times \frac{A_{1710}}{A_{1450}}$$

A_{1710} is the characteristic absorbance of carboxyls of grafted AA and A_{1450} is characteristic absorbance of CH_3 from PP backbone used as the reference band.

Table 1 The mechanical properties of the raw PP and PP-*g*-AA

sample	composition *m*(PP):*m* (rPP):*m* (AA)	G_d (%)	MFR[a] /g·10 min^{-1}	tensile strength[b] /MPa	elongation at break/%	notched izod impact resistance[c]/kJ·m^{-2}	T-Peel strength on Al substrate[d]/kN·m^{-1}
A	100:0:0	0	3.3	26.8	220.7	9.0	0
	95:5:0.8	0.1	3.3	26.1	199.3	8.3	0.26
	92:8:0.8	0.17	4.1	26.4	203.1	8.6	0.57
	90:10:0.8	0.19	5.6	26.8	249.3	10.4	4.88
	85:15:0.8	0.27	7.2	26.4	183.1	8.6	5.34
	80:20:0.8	0.32	7.4	26.5	152.4	8.4	6.51
B	90:10:0	0	8.8	23.0	117.8	7.1	0
	90:10:0.6	0.16	5.0	26.2	155.0	8.0	0.68
	90:10:0.8	0.19	5.6	26.8	249.3	10.4	4.88
	90:10:1.0	0.28	2.9	26.7	207.3	10.3	5.10
	90:10:1.5	0.44	1.0	27.5	165.7	10.2	5.04
	90:10:2.0	0.39	0.5	26.9	139.8	12.0	7.25

[a] 230°C, 2.160 kg; [b] GB/T 1040−92, 50 mm/min of tensile ate; [c] GB/T 1843−1996, 2.54 mm of notched depth; [d] GB/T 2790−1995, 50 mm/min of crosshead rate

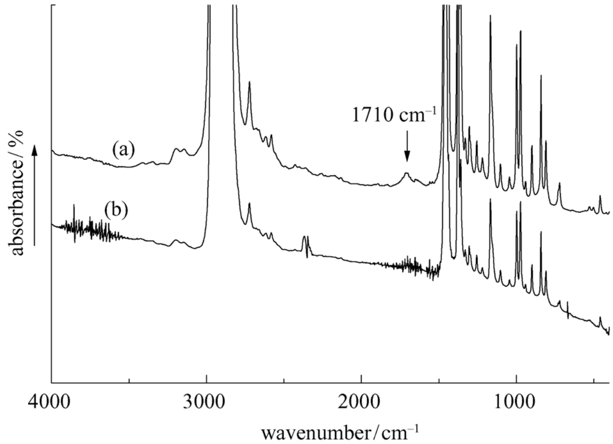


Fig. 1 The FIIR spectra of (a) neat PP and purified (b) PP-*g*-AA

3.2 Structure and morphology of PP-*g*-AA

The DSC thermograms of raw PP and PP-*g*-AA is presented in Fig. 2, where the crystallization during cooling from 200°C and the subsequent melting runs are shown. Compared to those of raw PP, the enhancement of crystallization and melting temperature of PP-*g*-AA was observed, which can be explained as follows: the presence of branches (graft chain) within a linear PP chain acts as the nucleation agent, and they increase the crystallization temperature and crystallization rate simultaneously, resulting in the thick crystal and subsequent high melting temperature [7].

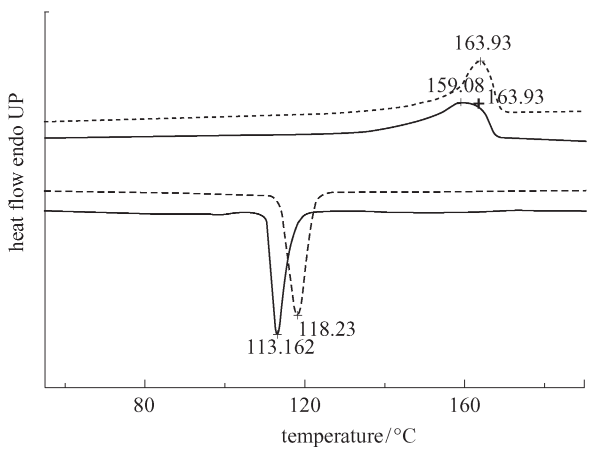


Fig. 2 DSC thermograms of raw PP(solid line) and PP-*g*-AA (dash line)

The crystalline morphology of raw PP and PP-*g*-AA ($G_d = 0.19\%$) is presented in Fig. 3. the raw PP exhibits a common spherulitic structure and interfaces between the spherulites are sharp and clear, while the grafted PP shows the blurry interfaces between the spherulites. These results are in agreement with the DSC observations.

3.3 The effect reaction parameters on grafting reaction

The effect of irradiation dose on the grafting reactions is presented in Fig. 4. The monomer concentration is 0.8 wt% and the composition (PP/rPP/AA) is 90/10/0.8. The G_d of PP-*g*-AA decreases with the increasing irradiation dose and then levels off. Since the high G_d results in good mechanical properties, the irradiated PP with 4 kGy dose is used as initiator for further studies.

The effect of ratio of rPP to PP on the grafting reaction is represented in Fig. 5. The monomer concentration is 0.8 wt%. The G_d of PP-*g*-AA increases with the increasing load of rPP is observed, which can be attributed to the increased initiator concentration and corresponding to the concentration of free radicals that are capable of initiating the grafting reaction.

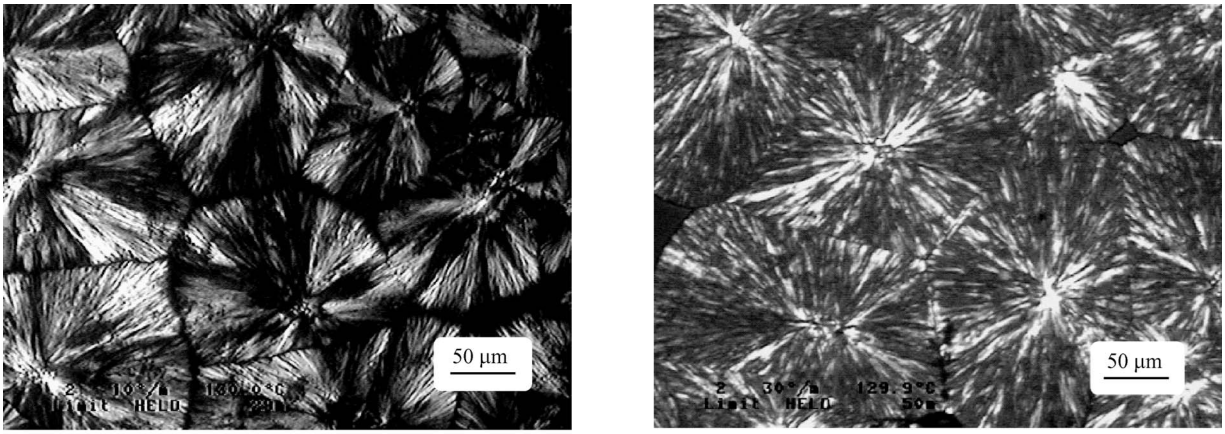
The effect of AA concentration on the grafting degree is presented in Fig. 6. The ratio of rPP to PP is 1/9. The G_d increases with the increasing AA concentration first, then reaches the maximum and decreases with further increments in the AA concentration. This tendency can be explained as follows: the local monomer concentration increases as the result of increasing feed monomer concentration, which favors the grafting reaction in the melt. On the other hand, the monomer aggregates readily at high concentrations [8] and favors the homopolymerization. The competition between the homopolymerization and grafting reaction results in the maximum of G_d.

3.4 The properties of PP-*g*-AA

The mechanical test results of PP and PP-*g*-AA are listed in Table 1. In the A series of samples, the MFR of PP-*g*-AA increases with increasing rPP concentration and the tensile strength, elongation at break and notched impact strength reach the maximum when the ratio of rPP to PP is 1/9. This suggests that the increasing concentration of rPP (similar to peroxide initiator) induces the grafting reaction and degradation simultaneously [7] and the presence of rPP with the low molecular weight also degrades the mechanical properties.

The effects of monomer concentrations on the mechanical properties were investigated in the B series of samples. Serious degradation of the samples without adding AA monomer was observed. The presence of monomer suppresses the degradation, resulting in the decreased MFR and increased notched impact strength. The reduced spherulite size and increased lamellar thickness in the grafted PP are the main reasonsfor the increased mechanical properties.

Because carboxylic group was introduced to the PP backbone uniformly, it was expected to have good adhesion with polar substrates such as metal and glass [9]. So the adhesive strength of PP-*g*-AA to aluminium sheet and the 180° T-peel strength, was checked for the grafted product. It was found that the 180° T-peel strength increased with the



(a) (b)

Fig. 3 Comparison of crystalline morphology between raw PP(a) and PP-*g*-AA(b)

increasing G_d, and it has greatly increased to 6.51 KN/m which is a remarkable improvement.

As shown in Table 1, the product with higher G_d (0.19%) and relatively excellent mechanical properties can be produced if the mass ratio of PP/rPP/AA is 90:10:0.8 where selected pre-irradiation dose of rPP is 4 kGy.

3.5 Mechanism

When PP is pre-irradiated by EB in air, the trapped radical and peroxide or hydroperoxide are created simultaneously. The trapped radical is decays easily at room temperature while the peroxide and hydroperoxide are stable and can be stored for days or even months [2]. The principle is shown in step 1.

$$\mathrm{PP} \xrightarrow[\mathrm{O_2}]{\text{electron beam}} \mathrm{POOP\ or\ POOH} \tag{1}$$

When heat and shearing, etc. are applied, the macroperoxide will decompose to yield alkyl and hydroxyl radicals. These radicals attack the matrix chain and preferentially abstract a tertiary hydrogen atom [10]. Inter-chain H abstraction and intra-chain H-abstraction will occur simultaneously and a secondary free radical is formed (step 2, 3) [11].

$$\mathrm{POOP\ or\ POOH} \longrightarrow \mathrm{PO\cdot + \cdot OH} \tag{2}$$

$$\mathrm{PO\cdot + PP} \longrightarrow \mathrm{PP\cdot + P-OH} \tag{3}$$

The relatively long life of this kind of secondary free radial increases the probability of grafting reactions and reduces the probability of degradation which is the pivotal to obtain the functionalized PP with good mechanical properties (step 4).

$$\mathrm{PP\cdot + M} \longrightarrow \mathrm{PP-M} \tag{4}$$

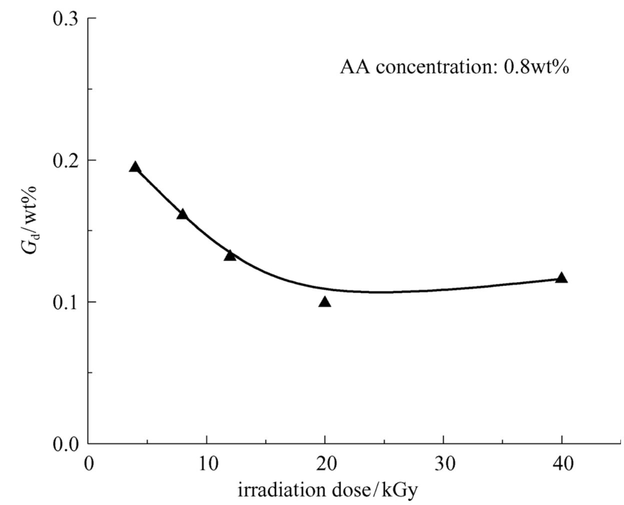


Fig. 4 The effect of irradiation dose of rPP on G_d (rPP/AA/PP = 10/1/90)

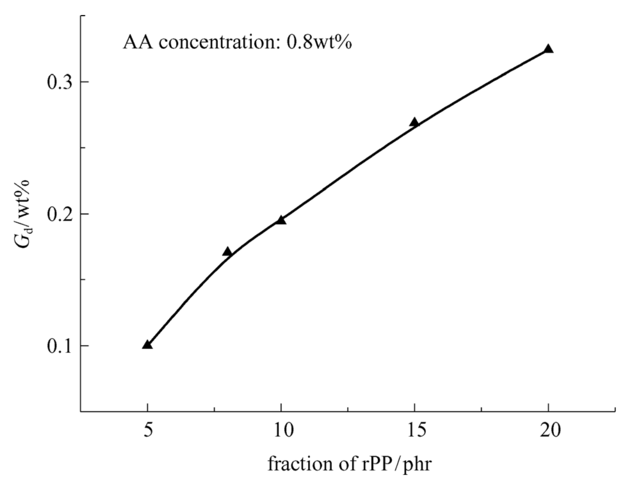


Fig. 5 The effect of fraction of rPP on G_d

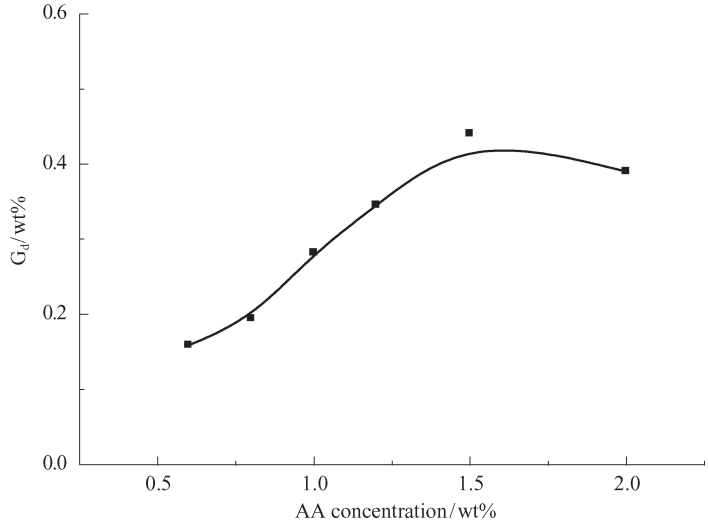


Fig. 6 The effect of AA concentration on G_d

References

1. Chen J, Nho Y C, Park J S. Radiat Phys Chem, 1998, 52: 201
2. Chen J, Yang L M, Chen L Q, et al. Radiat Phys Chem, 2004, 69(2): 149
3. Chen D T, Shi N, Xie L Q, et al. Acta Polym Sin, 2000, 1: 32
4. Ha H F, WU J L. Radiation Chemistry in Polymer: Principle and Applications, Beijing: Peking University Press, 2002: 59
5. Rivaton A, Lalande D, Gardette J L. Nucl Instrum Methods Phys Res Sect B-Beam Interact. Mater. Atoms, 2004, 222: 187
6. Cai C L, Shi Q, Zhu L C, Yin J. Chem J Chinese Univers, 2006, 27(10): 1969
7. Mai K C, Li Z J, Zeng H M. J Appl Polym Sci, 2001, 80(13): 2609
8. Nath S K, De Pablo J J. J Phys Chem B, 1999, 103(18): 3539
9. Lin C W, Lee W L. J Appl Polym Sci, 1998, 70(2): 383
10. Shi Q, Cai CL, Zhu LC, Yin J. Polymer, 2007, 47(6): 1979
11. Tobita H, Zhu S P. J. Polym Sci Part B, 1996, 34 (12): 2099