



## Study of Mechanical Properties and Morphology of PA 6/PO Blends Compatibilized by PO Grafted with Itaconic Acid

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**Abstract:** Two different types of polyolefine (PO) grafted with itaconic acid as a reactive compatibilizer, polypropylene (PP) grafted with itaconic acid (PP-*g*-ITA) and high density polyethylene (HDPE) grafted with itaconic acid (HDPE-*g*-ITA), PP and HDPE grafted with copolymer of itaconic acid and styrene (PP-*g*-(ITA-St) and HDPE-*g*-(ITA-St)) were prepared by melt graft technique through reactive type twin-screw extruder. FT-IR and thermal analysis were used to characterize the structure of the graft copolymer. The graft ratio (GR) and melt flow rate (MFR) were determined by non-aqueous titration and melt flow rate analyzer. The effect of the concentration of monomer and initiator dosage on GR and MFR of graft copolymer were studied. Then polyamide 6 (PA 6) blends, PA 6/PP (PA 6/HDPE), that compatibilized with PP-*g*-ITA (HDPE-*g*-ITA) were prepared. The morphology of the blends was analyzed by SEM, DSC and Molau tests and the mechanical properties of which were characterized by tensile, impact, and bend tests. The results of mechanical property showed that the impact strength of blends was increased by 50% and 70% after PP-*g*-ITA and HDPE-*g*-ITA was used as compatibilizer, but the MFR of blends was decreased. The SEM photographs indicated that the accession of compatibilizer obviously improved binding state between two phases in blends, the size of dispersed phase was reduced evidently and the interface became indistinct. DSC results demonstrated that in the case of PP-*g*-ITA, glass temperature ( $T_g$ ) of PA 6 matrix in blends was ascended, melt point ( $T_m$ ) was improved a little, crystallinity ( $X_c$ ) was decreased,  $T_m$  and  $X_c$  of PP phase was increased; With the accession of HDPE-*g*-ITA,  $T_m$  of PA 6 matrix and HDPE phase had almost no change,  $X_c$  of PA 6 matrix was decreased and  $X_c$  of HDPE phase was increased.

**Keywords:** PA 6, PO, Blend, Compatibilizer; ITA.

### Introduction

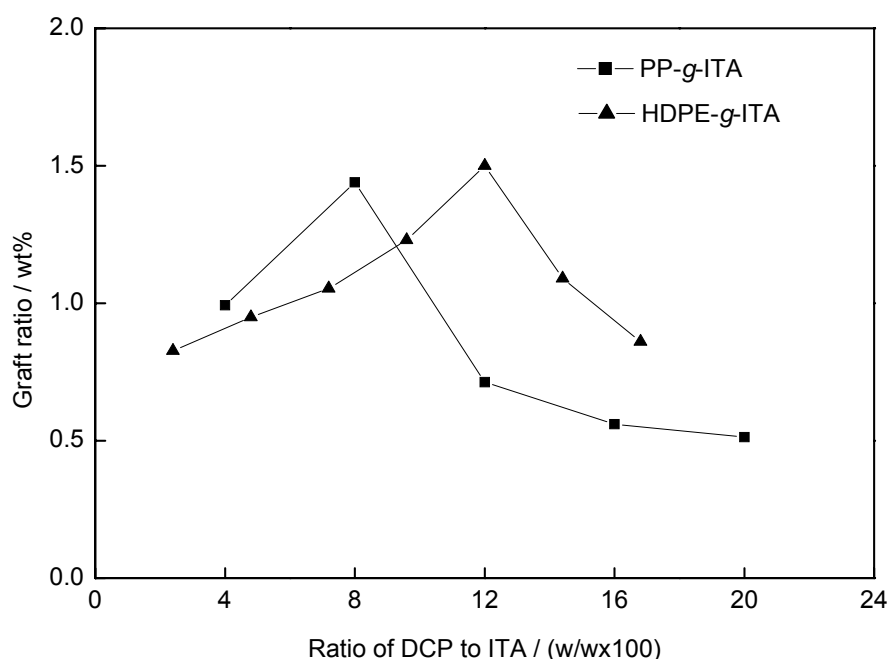
Polyamide 6 (PA 6) is used widely as a sort of engineering plastic. But it is very brittle, especially when some defects exist, which restricts its application. Many researchers tried to improve the brittleness of PA 6 [1], for example, thermoplastics (PP, PE, copolyester etc.) [2-4], rubber elastomer (POE, SEBS, EVA, EPR, PPE, semicrystalline elastomer etc.), core-shell latex particle (MBS, PBA/PMMA, TPEg, PB/PMMA etc.) and so on were used to toughen PA 6, which can enhance the impact strength of PA 6 observably. Two major factors influence the performance of blends in the process of toughening modification: First, PA 6 is generally incompatible with toughening phase, which will lead to phase separation. Second, It is very important

that whether toughening phase can be dispersed homogeneously in PA 6 matrix or not. The size of dispersed phase had better be controlled in the range of 0.2~0.3  $\mu\text{m}$ . For such purpose, the third phase such as SMA copolymer or DGEBA epoxy resin [12, 15] were used as compatibilizer and added into the blend system of PA 6 and toughening phase. The compatibilizer usually exists in the interface of matrix and dispersed phase [16-17]. The reason of compatibilizer improving the impact strength of blend is due to the chemical reaction between maleic anhydride (MAH) which exists in the interface and the end amino group of PA 6. So far MAH graft copolymers are used as major compatibilizer in research field and the production of PA 6 alloy [2, 7-9, 12, 18-22]. Usage of MAH as a graft monomer has a big limitation because of its great toxicity, low boiling point of 220  $^{\circ}\text{C}$  and easy sublimation. In the process of melt graft, the volatilization of MAH will damage the operator eyes. Compared to MAH, itaconic acid (ITA) is more suitable to be used as compatibilizer due to its higher melt and boiling point, which makes it not easy to volatilize and decompose in the graft process. Also, it has unsaturated double bond and carboxyl group which can react with the end amino group of PA 6. Therefore, we are interested in melt graft of PP (HDPE) with ITA and its application in PA 6/PP (PA 6/HDPE) alloy system.

## Results and Discussion

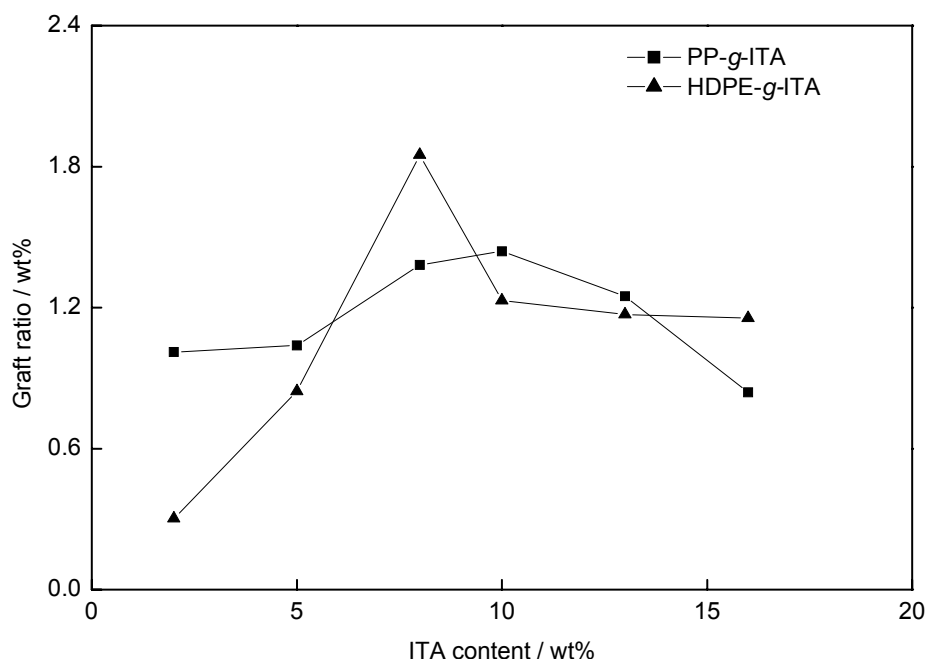
### Grafting Modification of PO

As shown in Figure 1, with the increase of dicumyl peroxide (DCP) content, GR of PP-*g*-ITA and HDPE-*g*-ITA increased to a peak value and then decreased. With the increase of initiator DCP content, the concentration of PO macromolecular free radical ascended; graft speed and GR enhanced, too.



**Fig. 1.** Effect of DCP content on graft ratio (GR) of PO (ITA/PO = 1/9).

For PP, when the ratio of DCP to ITA (w/w) increased to 0.08, GR reached the maximum of 1.44 wt%; and for HDPE, when the ratio of DCP to ITA (w/w) increased to 0.10, GR reached the maximum of 1.50 wt%. After that, GR began to decrease, MFR of PP-*g*-ITA increased rapidly and MFR of HDPE-*g*-ITA decreased rapidly, which may due to the aggravation of side reactions such as degradation of PP and cross linking of HDPE.

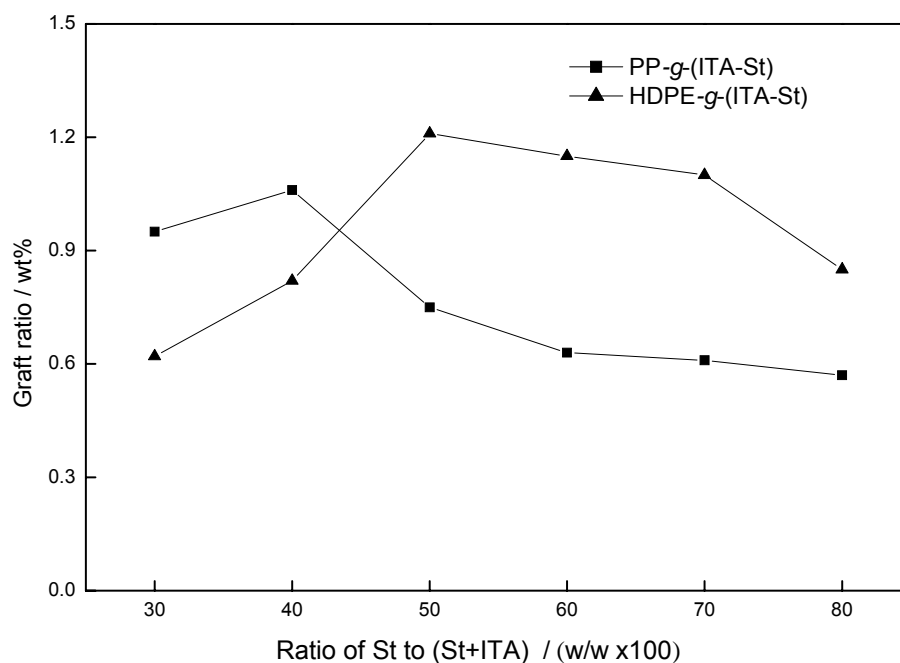


**Fig. 2.** Effect of ITA content on graft ratio (GR) of PO.

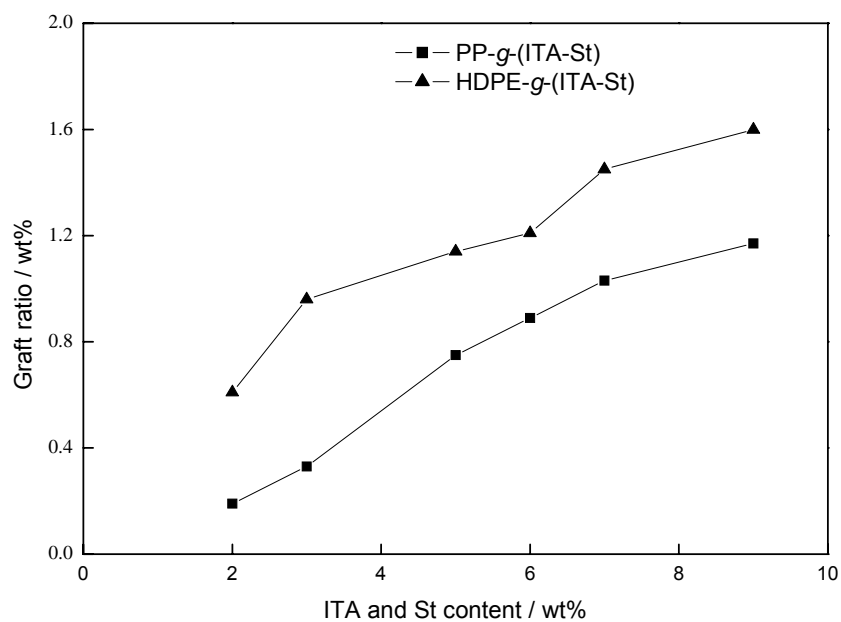
In Figure 2, proportion of DCP to ITA was fixed, DCP/ITA = 8/100 for PP, DCP/ITA = 10/100 for HDPE. With the increase of ITA content, the changing tendency of GR of PP-*g*-ITA and HDPE-*g*-ITA were similar. For PP, when ITA content increased to 10 wt%, GR reached the maximum of 1.44 wt%; and for HDPE, when ITA content is 8 wt%, GR reached the maximum of 1.85 wt%. After that, GR begun to decrease gradually, it may be due to the same reason as above and the homo-polymerization of ITA.

From Figure 3 it can be seen that GR increased to peak value 1.06 wt% when St content reached 0.40 wt% for PP and GR increased to maximum 1.20 wt% when St content reached 0.50 wt% for HDPE, then GR begun to decrease gradually. Because of increase of St content, the proportion of ITA to PP (HDPE) decreased which led to the decrease of GR. on the other hand, the efficiency of ITA graft reaction enhanced on account of the participation of St in copolymerization, which led to GR increase. In fact, the single peak curve in Figure 3 resulted from co-action of two factors. When St content reached 0.40 wt%, PP/ITA = 100/3.6, GR of PP-*g*-ITA is about 1.04 wt% at same proportion, that means the effect of St on GR in preparation of PP-*g*-(ITA-St) is not obvious. Under the same condition, changing St content to 0.50 wt%, HDPE/ITA = 100/3, GR of HDPE-*g*-ITA was decreased to 0.6 wt%, which indicated that the introduction of St enhanced the ability of ITA grafting HDPE evidently. As shown in

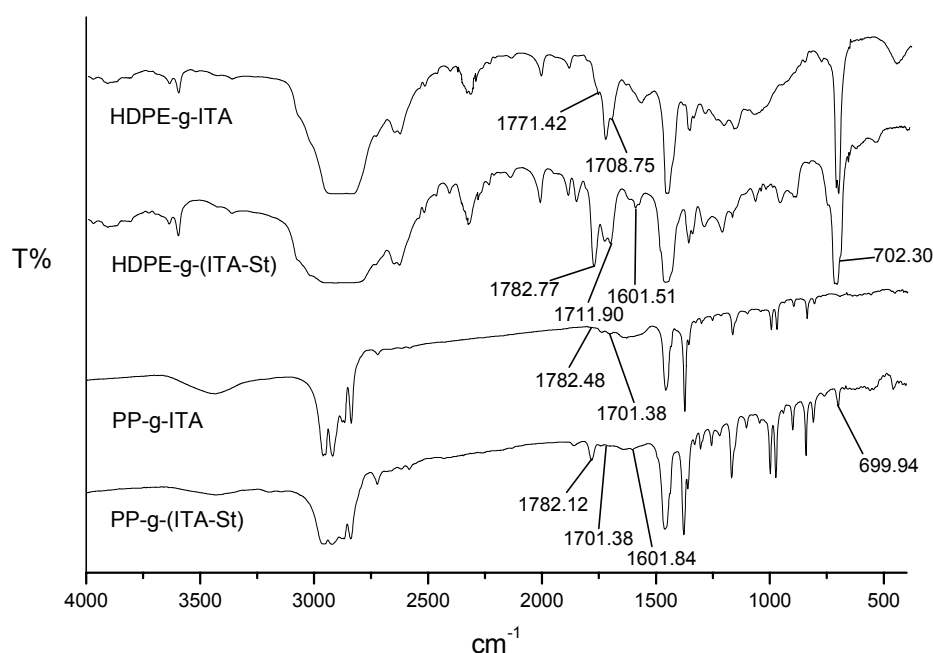
Figure 4, GR is increased gradually with the increase of monomer content.



**Fig. 3.** Effect of St content on graft ratio (GR) (PP/ (ITA+St) /DCP = 100/6/0.6).

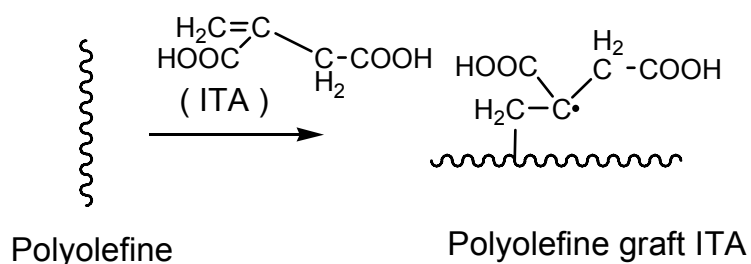


**Fig. 4.** Effect of monomer (ITA+St) content on graft ratio (GR) (ITA/St/DCP = 1/1/0.2).



**Fig. 5.** FT-IR spectra of graft copolymer.

In normal case, the absorb peak of carboxyl of ITA will appear at  $1703.62\text{ cm}^{-1}$ . Figure 5 shows that the carboxyl absorb peak of PP-g-ITA was transferred to  $1701.38\text{ cm}^{-1}$ , which proved that monomer ITA has been grafted to the main-chain of PP successfully. Because of the variety of ITA bond structure and PP aggregative structure, the absorb peak of carboxyl shifted to long wave. Monomer ITA and St were deduced to be grafted to main-chain of PP by the strong absorb peaks at  $1782.12\text{ cm}^{-1}$  and  $699.94\text{ cm}^{-1}$ , which showed the existence of anhydride and benzene ring. During the grafting process, the carboxyl group of ITA was dehydrated to anhydride at high temperature and pressure, as a result the carboxyl peak weakened. The absorption peak at  $1782.12\text{ cm}^{-1}$  near  $1701.38\text{ cm}^{-1}$  was also assigned to be anhydride group, which indicated that the phenomenon of ITA dehydration to anhydride existed in the process of PP-g-ITA preparation, too. The peaks at  $1706.75\text{ cm}^{-1}$  and  $1711.90\text{ cm}^{-1}$  showed monomer ITA was grafted to the main-chain of HDPE successfully. Perhaps the blue shift of carboxyl group was caused by the change of bond structure of monomer ITA, aggregate structure of HDPE and the copolymerization of ITA with St. The weak carboxyl peak of HDPE-g-(ITA-St), the strong anhydride peak at  $1782.77\text{ cm}^{-1}$  and the typical benzene peaks at  $702.30\text{ cm}^{-1}$ ,  $758.91\text{ cm}^{-1}$  and  $1601.51\text{ cm}^{-1}$  suggested the carboxyl group of ITA was dehydrated to anhydride because of the high temperature and pressure in graft process, leading to the weakening of absorption of carboxyl and intensifying of absorption of anhydride. Similarly, the absorb peak of anhydride was also found at  $1771.42\text{ cm}^{-1}$  in spectra of HDPE-g-ITA, which meant the phenomenon of ITA dehydration to anhydride also exist in the process of HDPE-g-ITA preparation. The absorb peak of anhydride of PP-g-ITA (HDPE-g-ITA) is weaker than that of PP-g-(ITA-St) (HDPE-g-(ITA-St)). Obviously, we can assume that dehydrate-to-anhydride reaction intensified owing to introduction of St and the dehydration of ITA occurred is intra-molecular.

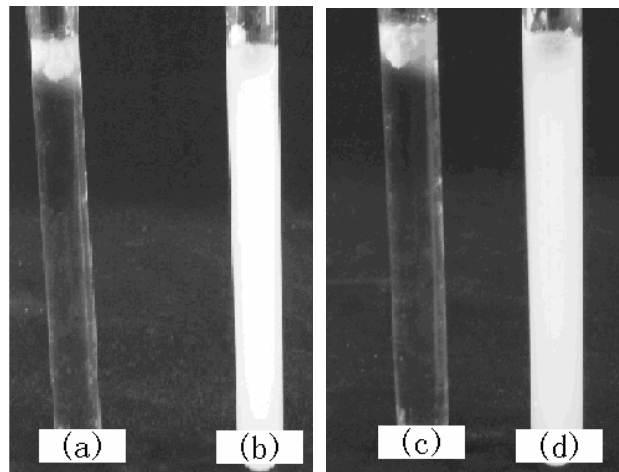


**Tab. 1.** Thermal Analysis Data.

| Specimens  | $T_m(^{\circ}\text{C})$ | $T_d(^{\circ}\text{C})$ |
|------------|-------------------------|-------------------------|
| ITA        | 162.4                   | —                       |
| PP         | 159.5                   | 437.6                   |
| PP-g-ITA   | 157.6                   | 441.3                   |
| HDPE       | 127.2                   | 461.0                   |
| HDPE-g-ITA | 124.3                   | 461.8                   |

The melting point ( $T_m$ ) was decreased and decomposition temperature ( $T_d$ ) was increased a little after PO was grafted with ITA (Table 1). It is because of the disadvantageous effect of grafting side-chain on regular arrangement of PO molecule chain in crystal lattice and the enhancement of intermolecular force due to introduction of polar group in PO molecule chain.

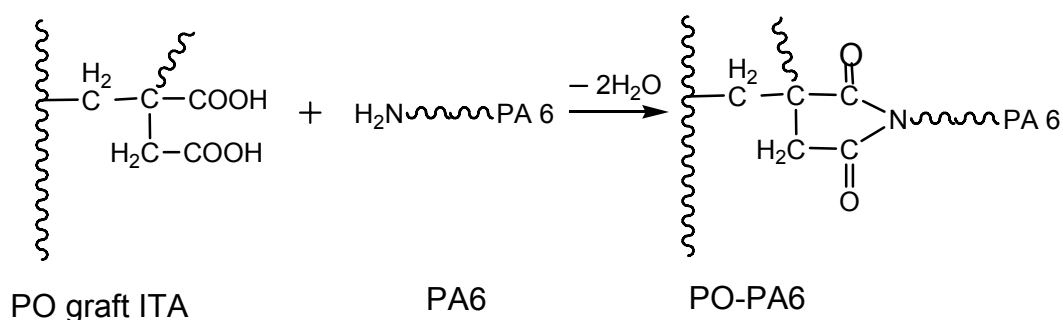
#### *Molau Experiment.*



**Fig. 6.** Photograph of Molau experiment. (a) PA 6/PP; (b) PA 6/PP/PP-*g*-ITA; (c) PA 6/HDPE; (d) PA 6/HDPE/HDPE-*g*-ITA

Molau experiment is used as a simple and effective method to inspect compatibility of blend interface. As we all know that pure PA 6 can be dissolved in formic acid to give a transparent solution, but PP and HDPE cannot be dissolved in formic acid. We dissolved a little of PA 6/PP, PA 6/PP/PP-*g*-ITA, PA 6/HDPE and PA 6/HDPE/HDPE-*g*-A in formic acid, respectively, then observed the solubility (Fig. 6). The results showed that in the case of binary blend of PA 6/PP, PA 6 matrix was dissolved completely to form a transparent solution in a few hours but PP phase was separated out and floated on the surface of solution. This phenomenon of phase

separation demonstrated that the cohesive force between two phases was very weak. When ternary blends PA 6/PP/PP-*g*-ITA and PA 6/HDPE/HDPE-*g*-ITA were dissolved in formic acid, both blends were dissolved in formic acid to form emulsion which could not be separated by filtration. This result showed that the carboxyl group (or anhydride group) in graft copolymer occurred a situ-reaction with amino group existing at the end of PA 6 molecular chain to give a new block copolymer which contains PA 6 and PO block simultaneously after adding ITA graft copolymer to blend system of PA 6/PO. The copolymer weakened interfacial tension and improved compatibility between two phases as a compatibilizer of blend system of PA 6/PO.

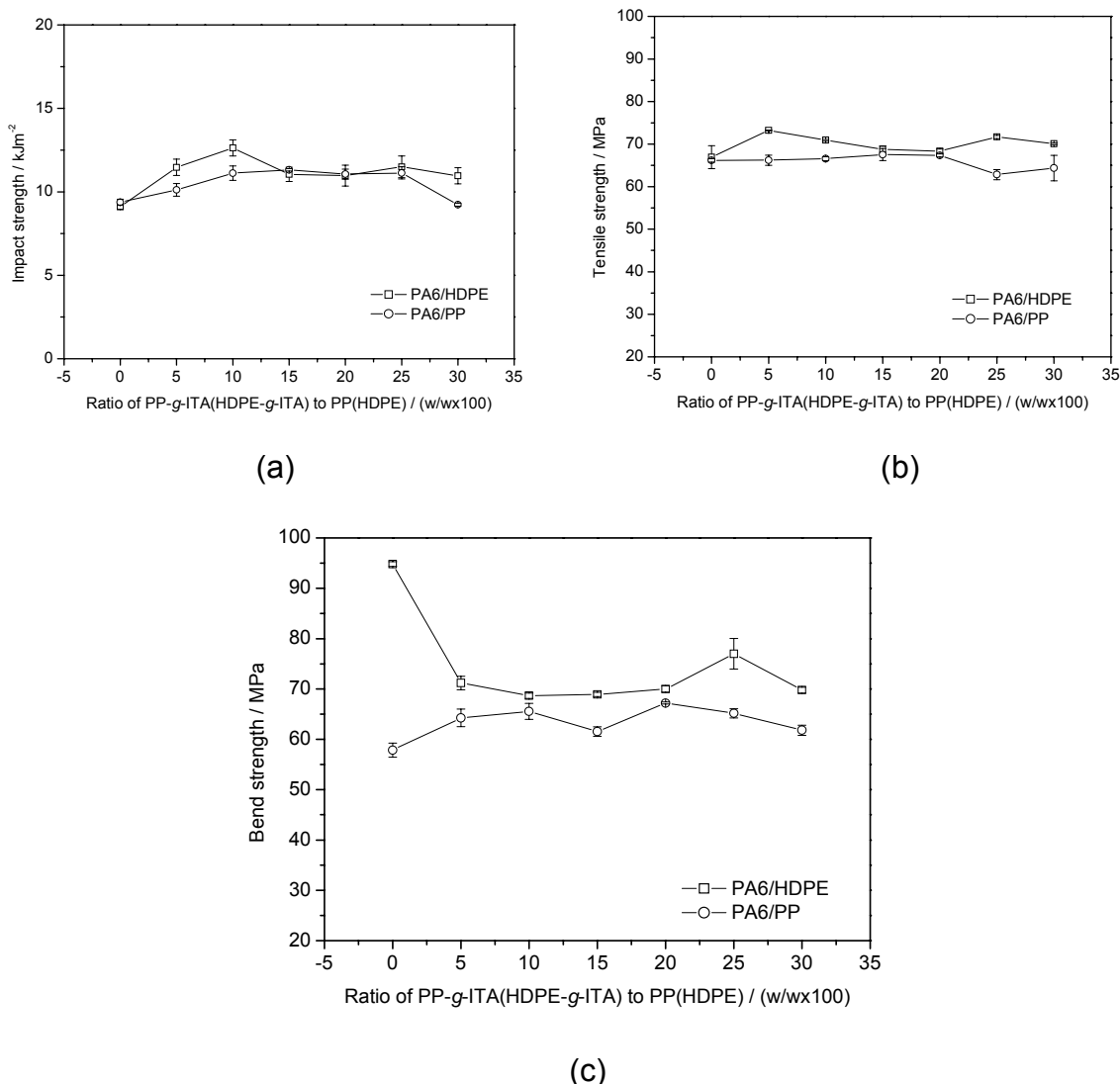


### *Relationship between Mechanical Property and Compatibilizer*

The impact strength of blend system PA 6/PO was improved obviously after PO-*g*-ITA addition (Figure 7 (a)). In the case of PA 6/PP/PP-*g*-ITA = 80/20/3, notched impact strength was 11.32 kJ/m<sup>2</sup> and 50% higher than pure PA 6. In the case of PA 6/HDPE/HDPE-*g*-ITA = 80/20/2, notched impact strength reached 12.63 kJ/m<sup>2</sup>, increased about 70% than pure PA 6. The blend process provided the reaction between carboxyl group and the end amino group of PA 6 to give a new block copolymer PA 6-*b*-PP (PA 6-*b*-HDPE). The two blocks of copolymer were compatible with PA 6 matrix and PO phase to form stable blend system. Then the thickening and reinforcing of interface and smaller size of dispersed phase enhanced the impact strength of the blend system. After graft copolymer added to a certain value, mechanical properties of blend could not be improved any more even if the amount of compatibilizer was increased. This suggested that the dimensions of change of dispersed phase would affect the mechanical properties of the blends in a certain way. When the size of dispersed phase reduced to a critical value, its influence on mechanical property was very small. So far, the best mechanical property was fitted with an optimal compatibilizer dosage. In such case the mechanical property could not be improved even if the morphology of the blends showed perfect result with the increased amount of compatibilizer. On the other hand, graft copolymer also had some side effects when compared to the blend. The mechanical properties of the graft copolymer prepared by melt graft only using ITA will be decreased because of the serious degradation of PP (cross linking of HDPE) in graft process. Hence, large amount of compatibilizer will lead to serious side effect and unexpected mechanical properties of blends.

Fig. 7 (c) showed that the influence of dispersed phase PP on the crystalline behavior of PA 6 matrix was bigger than dispersed phase HDPE. 20 wt% of PP had made the bend strength of blend PA 6/PP to decrease from 103.86 MPa to 57.85 MPa, but the blend PA 6/HDPE varied a little. Perhaps the above-mentioned results concerned the similar crystal structure of PA 6 and PP, both in monoclinic crystal system, which resulted in the mutual effect between PA 6 and PP to enhance. In the presence of

block copolymer PA 6-PP (PA 6-HDPE), the difference between the crystalline morphology of blends dwindled gradually. The effect of compatibilizer content on the bend strength of blends incline toward conformance. The tensile strength of blends had little change (Figure 7 (b)).



**Fig. 7.** Effect of compatibilizer dosage on mechanical property of PA 6/PO (PA 6/PO = 80/20 (w/w)).

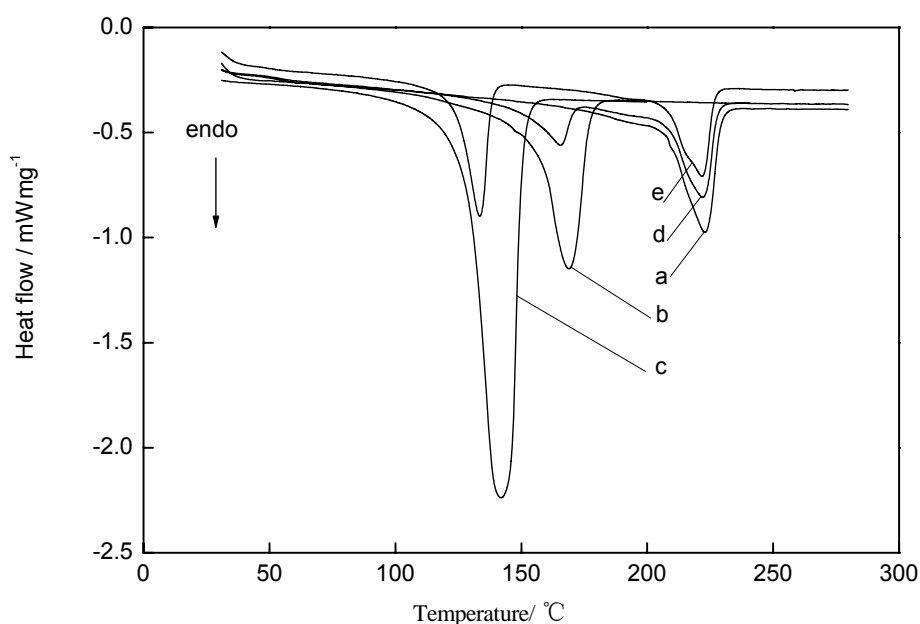
### Morphology Structure of Blends PA 6

#### -Melting behavior of blends PA 6

After introducing compatibilizer into blend system PA 6/PP,  $T_g$  of PA 6 matrix raised,  $T_m$  moved up a little and  $X_c$  lowered, but both  $T_m$  and  $X_c$  of PP phase was raised (Figure 8, Table 2). This result confirmed that there were some affect of PP-g-ITA on crystal behavior of blend. In the process of melt extrusion of ternary blend PA 6/PP/ PP-g-ITA, the block copolymer PA 6-PP was produced in situ-reaction. The end number of PA 6 molecular chain reduced and moving ability of PA 6 segment lowered, which led to rise of  $T_g$  of PA 6 matrix. Reduction of moving ability of PA 6 segment could influence molecular chain to conquer lattice energy and transform from order to disorder, which



caused little increase of  $T_m$  of PA 6 matrix. About PP phase, the raising of  $T_m$  was also caused by the same reason mentioned above, but the effect was bigger than that on PA 6 matrix.



**Fig. 8.** DSC curves of blends PA 6/PO. a PA 6; b PP; c HDPE; d blend PA 6/PP/PP-*g*-ITA; e blend PA 6/HDPE/HDPE-*g*-ITA.

The strong intermolecular force of PA 6 segment in block copolymer PA 6-PP made the disordering of molecular chain of PP phase to be finished at much higher temperature. With respect to the forming of block copolymer, PA 6-PP induced a part of PA 6 to move to interface layer of phases followed with PA 6-PP. This part of PA 6 did not participate in crystal formation. Therefore,  $X_c$  of PA 6 matrix was decreased. On the contrary, the strong intermolecular action of PA 6 block chain of PP-PA 6 induced and improved crystal of PP phase, which led to higher  $X_c$ .

**Tab. 2.** Thermal Analysis of Blend PA 6/PP/PP-*g*-ITA.

| Specimens                       | $T_m$ (°C)  |          | $T_g$ (°C)  | $X_c$ (%)   |          |
|---------------------------------|-------------|----------|-------------|-------------|----------|
|                                 | PA 6 matrix | PP Phase | PA 6 matrix | PA 6 matrix | PP Phase |
| Pure PA 6                       | 222.9       | -        | 55.8        | 22.97       | -        |
| Pure PP                         | -           | 168.8    | -           | -           | 40.85    |
| Blend PA 6/PP                   | 221.5       | 164.6    | 51.6        | 22.01       | 31.71    |
| Blend PA 6/PP/PP- <i>g</i> -ITA | 222.0       | 165.6    | 53.9        | 18.41       | 36.10    |

After adding compatibilizer to blend system PA 6/HDPE,  $T_m$  of PA 6 matrix and HDPE phase had almost no change,  $X_c$  of PA 6 matrix lowered and  $X_c$  of HDPE phase raised, but both  $T_m$  and  $X_c$  were lower than that of pure PA 6 and pure HDPE, respectively (Figure 8, Table 3). The influence of compatibilizer HDPE-*g*-ITA on  $T_m$  of blend was

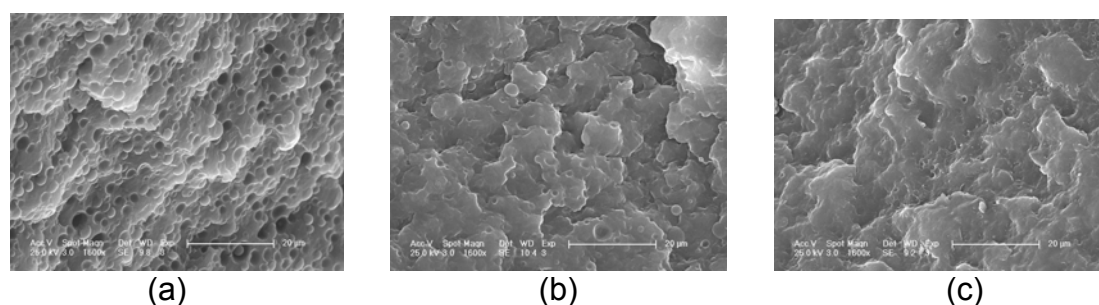
very little, but on  $X_c$  was big. This results show that HDPE-g-ITA did not influence the crystal structures of PA 6 matrix and HDPE phase so much. The block copolymer PA 6-HDPE was produced in situ-reaction in the process of melt extrusion, which restricted the movement of PA 6 molecular chain and led to decline both in crystal ability and crystal perfect degree of PA 6 matrix. Simultaneously, PA 6-HDPE could be used as crystal nucleus to enhance  $X_c$  of HDPE phase.

**Tab. 3.** Thermal Analysis of Blend PA 6/HDPE/HDPE-g-ITA.

| Specimens                  | $T_m$ ( $^{\circ}\text{C}$ ) |            | $T_g$ ( $^{\circ}\text{C}$ ) |             | $X_c$ (%)  |  |
|----------------------------|------------------------------|------------|------------------------------|-------------|------------|--|
|                            | PA 6 matrix                  | HDPE Phase | PA 6 matrix                  | PA 6 matrix | Phase HDPE |  |
| Pure PA 6                  | 222.9                        | -          | 55.8                         | 22.97       | -          |  |
| Pure HDPE                  | -                            | 141.9      | -                            | -           | 66.63      |  |
| Blend PA 6/HDPE            | 221.5                        | 134.6      | -                            | 20.43       | 55.15      |  |
| Blend PA 6/HDPE/HDPE-g-ITA | 222.0                        | 133.8      | 48.5                         | 18.95       | 61.10      |  |

### -SEM Analysis of Impact Fracture of Blend PA 6/PP

#### Analysis of Brittle Fracture

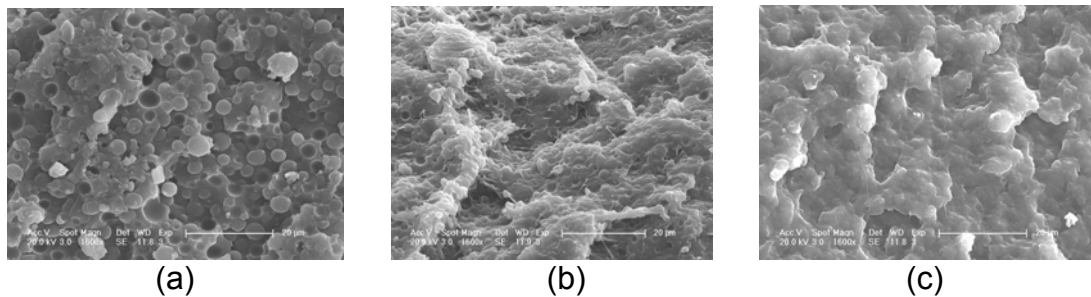


**Fig. 9.** SEM micrographs on the surfaces of brittle fracture of the blend PA 6/PP. (a) PA 6/PP=80/20, (b) PA 6/PP/PP-g-ITA=80/20/3, (c) PA 6/PP/PP-g-ITA=80/20/6.

SEM photographs of blend PA 6/PP (Figure 9 (a)) show that interface between PP dispersed phase and PA 6 matrix is very distinct and the size of dispersed phase is bigger and asymmetrical, which implicated that the blend system PA 6/PP was a double phase system with phase separation. After introducing PP-g-ITA (Figure 9 (b), (c)) to blend system, the size of dispersed phase decreased obviously and interface between PP dispersed phase and PA 6 matrix became indistinct, which suggested that the interaction in interface layer was improved. With the increase of PP-g-ITA dosage, the size of dispersed phase PP was further decreased, the dispersion phase became more homogeneous and interface almost disappeared. In the process of blend, carboxyl group of PP-g-ITA reacted with end amino group of PA 6 to form block copolymer PP-PA 6 and located mostly in the interface layer between PA 6 matrix and PP phase. PA 6 and PP block chain of PP-PA 6 were thermodynamically compatible with PA 6 matrix and PP phase, respectively, which resulted in decreasing of interfacial tension and increasing of cohesive force of interface obviously.

### Analysis of Impact Fracture

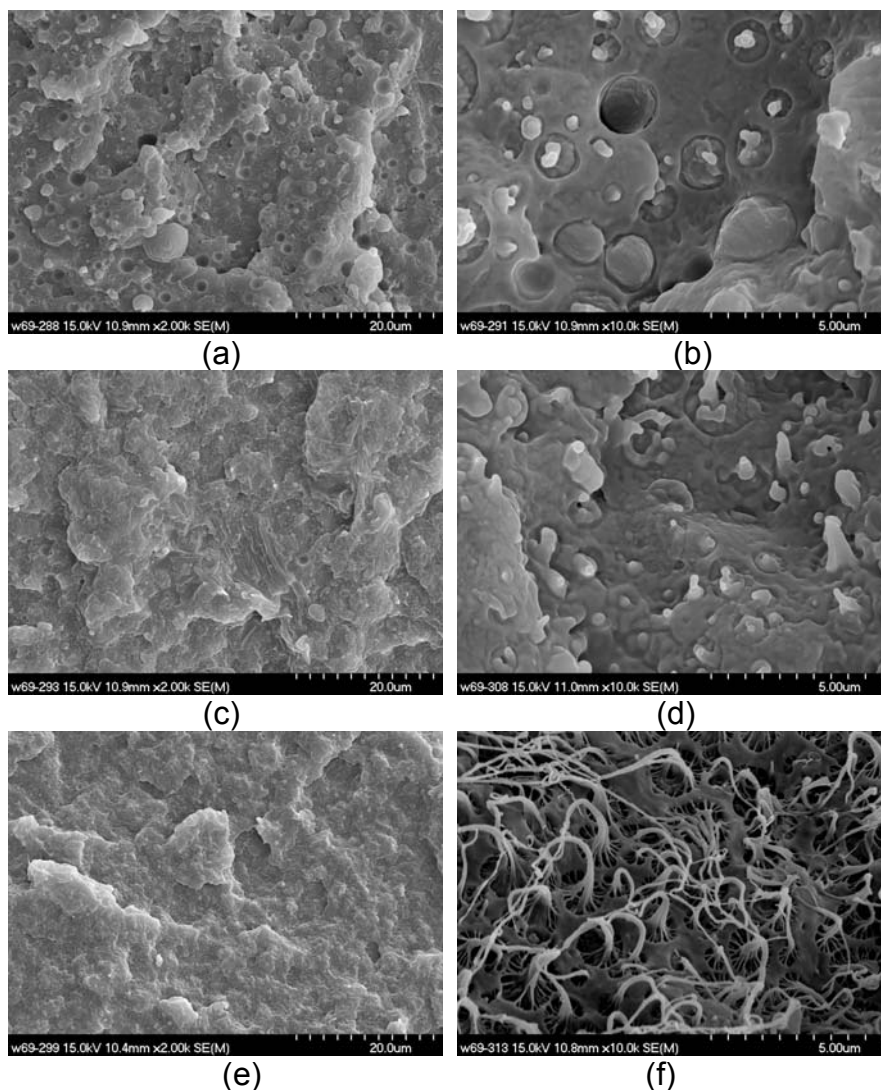
Figure 10 show SEM photographs of impact fracture of blend PA 6/PP containing different amount of PP-g-ITA. With the increase of PP-g-ITA dosage, the size of dispersed phase PP was decreased obviously and the conglutination of interface improved evidently. Following these results, the shape of dispersed phase particle was transformed from spheroid to ellipsoid, finally to column. The fibroid and gibbous substance appeared on the fracture surface; shearing deformation was evident pointing to ductile fracture. The above-mentioned facts accounted for that the stress could be transferred and dispersed efficiently when the specimens suffered impact. The plastic deformation had occurred, and a mass of impact energy was absorbed and consumed, which is why the deformation structure reason of impact strength of blend improved by large extent.



**Fig. 10.** SEM micrographs on the surfaces of impact fracture of the blend PA 6/PP. (a) PA 6/PP=80/20, (b) PA 6/PP/PP-g-ITA=80/20/3, (c) PA 6/PP/PP-g-ITA=80/20/6.

### -SEM Analysis of Impact Fracture of PA 6/HDPE

Deducing from SEM photographs of blends PA 6/HDPE (Figure 11 (a), (b)), interface between HDPE dispersed phase particle and PA 6 matrix was distinct. The size of HDPE phase was big and asymmetric. The results of high magnification microscope showed that the surface of impact fracture was very smooth and the fibriform protuberance was little, which revealed that this specimen was brittle fracture. In fact, all of these demonstrated that the blend PA 6/HDPE was a double phase system with phase separation obviously. After adding smaller amount of HDPE-g-ITA to blend system (Figure 11 (c), (d)), the size of dispersed phase HDPE decreased drastically, interface between dispersed phase particle and PA 6 matrix became blurry and interaction in interface layer was improved. According to the high magnification microscope, the knaggy surface of impact fracture showed the character of ductile fracture and the increasing fibriform substance indicated that plastic deformation could transfer and disperse the stress efficiently when the material suffered impact. Thus, the impact property of material was improved by large amount of impact energy absorbed and consumed. This is just the deformation structure reason of that impact strength of blend enhanced significantly. If adding more amount of HDPE-g-ITA (Figure 11 (e), (f)), the size of dispersed phase particle in blend was further decreased; dispersed phase became much homogeneous and interface almost disappeared. More fibriform substance was found when observing by high magnification microscope.



**Fig. 11.** SEM photographs on the surfaces of impact fracture of blend PA 6/HDPE. (a), (b) PA 6/HDPE=80/20; (c), (d) PA 6/HDPE/HDPE-*g*-ITA=80/20/2; (e), (f) PA 6/HDPE/HDPE-*g*-ITA=80/20/4.

## Conclusions

In the system of ITA melt graft PP, when PP/ITA/DCP = 90/10/0.8, GR of ITA reached maximum of 1.44 wt%. The second monomer St had little influence on GR of ITA. About HDPE system, when HDPE/ITA/DCP = 92/8/0.8, GR of ITA reached maximum of 1.85 wt%. The second monomer St had a big influence on GR of ITA, the maximum graft efficiency of ITA being when St/ITA = 1/1. The results of FT-IR spectra indicated that monomer ITA and St had been grafted to molecular chain of PP (HDPE). A part of carboxyl on ITA unit was dehydrated to anhydride, and the introduction of St intensified this reaction. In the case of PA 6/PP/PP-*g*-ITA = 80/20/3, the notched impact strength reached 11.32 kJ/m<sup>2</sup> and improved about 50% compared to pure PA 6. Changing the ratio to PA 6/HDPE/HDPE-*g*-ITA = 80/20/2, the notched impact strength of blend attained to 12.63 kJ/m<sup>2</sup> and 1.7 times of pure PA 6. The compatibilizer PP-*g*-ITA (HDPE-*g*-ITA) can improve interface cohesion of blend obviously. The interface became blurry, the size of dispersed phase decreased and the compatibility enhanced evidently. PP-*g*-ITA can improve *T<sub>g</sub>* of PA 6 matrix. Simultaneously, *T<sub>m</sub>* was

increased a little and  $X_c$  was reduced. But  $T_m$  and  $X_c$  of PP phase were enhanced. HDPE-*g*-ITA did not have any obvious influence on  $T_m$  of PA 6 matrix and HDPE phase in blends. But  $X_c$  of PA 6 matrix was reduced and  $X_c$  of HDPE phase was increased.

## Experimental part

### *Materials*

PA 6 (extrusion grade) was purchased from Longfei Nylon Engineering Plastics Factory (Heilongjiang, China). PP(No. T30S) and HDPE(No. 5000S) were commercial products of CNPC Corp. (Daqing, China). ITA (industry grade) was purchased from Langyatai Ltd. (Tsingtao, China). DCP (chemical purity) was purchased from Sinopharm Corp. (Shanghai, China). Other conventional reagents were used as received or purified by conventional methods.

### *Preparation of graft copolymer.*

In preparation process of PP-*g*-ITA (HDPE-*g*-ITA), at first, we fixed the value of PP (HDPE) / ITA at 90/10 then adjusted value of DCP/ITA to find the best proportion of DCP/ITA. After that, the value of DCP/ITA was fixed at 8/100 for PP (10/100 for HDPE) then we changed proportion of PP/ITA (HDPE/ITA) to test. PP-*g*-ITA (HDPE-*g*-ITA) was prepared by melt grafting technique by reactive type twin-screw extruder on condition 160-200 °C and 80 r/min.

In preparation process of PP-*g*-(ITA-St) (HDPE-*g*-(ITA-St)), the value of PP (HDPE)/monomer gross (ITA+St)/DCP was fixed at 100/6/0.6 firstly, then we adjusted the value of St/ITA to find the best proportion. After that, we fixed St/ITA at 1/1 followed with value change of PP (HDPE)/(ITA+St) to test. Melt grafting condition was the same as the above, monomer St was added into extruder through feeding hole by peristaltic pump.

### *Determination of characteristic parameter of graft copolymer.*

MFR was determined by melt flow rate tester according to GB3682-83. GR was examined by non-aqueous titration, which meant the weight percent of ITA in graft copolymer. Thermal analysis was carried out by TG/DTA (Pyris diamond, PE Corp., USA) with heating rate of 5 °C/min. FTIR (Spectrum-one, PE Corp., USA) was used to determine infrared absorption spectrum of specimens and KBr was used as carrier.

### *Preparation of blends*

Dry PA 6, PP (HDPE), PP-*g*-ITA (HDPE-*g*-ITA) and other assistant reagent were evenly mixed together in proportion firstly. Then the mixture was melted, extruded by twin-screw extruder at temperature range of 200-300 °C to give PA 6/PP/PP-*g*-ITA and PA 6/HDPE/HDPE-*g*-ITA blend respectively. After drying enough, the blend was molded to standard specimen for mechanical testing by injection-molding method.

### *Molau experiment.*

Addition of formic acid into test tubes which contained PA 6/PP, PA 6/HDPE, PA 6/PP/PP-*g*-ITA, and PA 6/HDPE/HDPE-*g*-ITA blend respectively, then dissolving status was observed.



### Testing of mechanical property

The impact strength was examined according to GB1043-79, tensile strength GB1040-79 with tensile rate of 50mm/min, and bend strength GB1042-79 with bend rate of 2 mm/min.

### DSC testing

At first, we heated the blends to 300 °C with heating rate of 10 °C /min, and then the heated blends were cooled to room temperature so as to eliminate thermal history of blends. After that, the blends were heated to 300 °C with heating rate of 10 °C /min again in order to observe melting behavior by use of DSC (DSC204 F1, Netzsch Corp., Germany).

### Observation with SEM

The blend PA 6/PP was broken off after embrittlement in liquid nitrogen and the morphology of section was observed with SEM (2000XMS, FEI Corp., USA) after gold-gilding in vacuum. And the morphology of impact section of blend PA 6/PP (PA 6/HDPE) was observed directly with SEM after gold-gilding of section in vacuum.

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