

## Preparation and Properties of 4, 4'-Diphenylmethane Diisocyanate Blocking Modified Poly(propylene carbonate)

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**ABSTRACT:** Poly(propylene carbonate) (PPC) is inferior in thermal stability and liable to incur thermal degradation, especially in the existence of residual bimetal catalyst. In this article, PPC containing residual catalyst was end-capped with 4, 4'-diphenylmethane diisocyanate (MDI) through melt compounding. The blends were characterized by infrared spectra, melt flow index (MFI), gel permeation chromatography (GPC), gel content measurement, thermogravimetric analysis, scanning electron microscopy, and tensile test. The effect of MDI on thermal stability, molecular weight, and tensile properties of PPC was studied. Thermal degradation kinetics of neat PPC and PPC+MDI blending samples was discussed with Friedman method. MFI, GPC, and gel content measurements showed that mainly end-capping reaction was carried out on PPC chains when 0.1% of MDI was added. However, as the amount of MDI exceeded to 0.3%, end-capping, chain-extension, and crosslinking reactions were synchronously carried out on PPC. Results showed that the end-capping, chain-extension, and crosslinking reaction occurring between PPC and MDI could effectively inhibit the unzipping degradation even when the residual catalyst was not removed thoroughly. When the content of MDI reached 1.0%, the initial degradation temperatures ( $T_{-5\%}$ ) increased from 176.26°C for neat PPC to 259.56°C. As a result, the processing temperature range and processing time were largely extended, and the heat resistance of PPC was improved remarkably. Meanwhile, the tensile property of the modified PPC was enhanced obviously. It may be due to the fact that the molecular weight and gel content of PPC were increased with the increasing amount of MDI. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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### INTRODUCTION

Green materials have become a vital global issue due to the increasing problems of environment and natural resources. Poly(propylene carbonate) (PPC) attracts great attention because of its biodegradation and effective carbon dioxide utilization during the manufacture. In addition, due to the properties of low-cost, transparency, and high elongation at break, as well as the excellent gas barrier property, PPC has great potential application in the development of plastic, elastomer, fiber, adhesive, and so on.

Although PPC has a promising prospect, its mechanical properties and thermal stability still need to be greatly enhanced for further applications. To improve its mechanical properties, some modifications have been made via melt blending with other polymers, such as polylactic acid, polyhydroxyalkanoates,

ethylene/vinyl alcohol copolymer, poly(vinyl chloride), and rubber, etc.<sup>1–7</sup> Unfortunately, most blending of the resins are performed at temperatures higher than 150°C with melting time over 10 min in the manufacturing process. PPC is highly sensitive to the manufacturing temperature and proceeding time. When it was blended with these polymers, PPC would be degraded obviously under such a rigorous condition, which resulted in a great decrease in molecular weight and melt viscosity of PPC. As a result, a poor blending effect and serious surface adhesion was inevitable. Therefore, the poor thermal stability of PPC gives rise to the unfavorable effect on the blending and brings about obstacles in the general equipments of manufacture.

Many studies have been carried out to investigate the degradation mechanism of PPC and improve its thermal stability.

Inoue<sup>8</sup> and Kuran<sup>9</sup> reported the degradation behavior of PPC at high temperature with or without residual organometallic catalysts. The neat PPC without residual catalysts thermally degraded in two steps: the random scission reaction of the chain, followed by the unzipping reaction to release cyclic carbonate, as shown in Figure 1. In chain unzipping, as shown in Figure 1(B), neat PPC would form a five-member cycle ending via the terminal hydroxyl group, resulting in the degradation of PPC chains. The residual catalysts could induce and accelerate the unzipping degradation of PPC at a relatively lower temperature. Liu<sup>10</sup> also found that the remaining of bimetal catalysts could induce the unzipping degradation of PPC even at room temperature. In addition, Meng and coworkers<sup>11,12</sup> demonstrated that PPC would process a random chain scission with temperature increment after removing the catalysts. With further increase in temperature, unzipping degradation reaction occurred. However, under the condition of high temperature and with residual catalysts, unzipping degradation played a critical role during PPC thermal degradation, which resulted in a poor thermal stability of PPC.

The terminal hydroxyl group of PPC is a key factor affecting the unzipping degradation of PPC.<sup>10</sup> The thermal stability of PPC can be enhanced via the end-capping of hydroxyl groups. Dixon<sup>13</sup> utilized organo-phosphorous compounds and isocyanates to react with hydroxyl groups, resulting in inhibition of unzipping degradation through forming of inert functional groups. Additionally, Peng<sup>14</sup> reported a method to modify PPC with some end-capping agents, such as anhydride, benzoyl chloride, ethyl silicate, phosphoryl chloride, and so on. With the role of end-capping, the stability of PPC was significantly enhanced. In particular, 5% weight loss temperature increased by 30°C–60°C. Furthermore, Lai<sup>15</sup> and Xiong<sup>16</sup> found that maleic anhydride and its macrocycle radical copolymers could enhance the thermal stability of PPC. Meanwhile, maleic anhydride brought about intercoupling in macromolecules, and an increase in molecular weight of PPC, resulting in enhancement of the thermal stability of PPC.

To the best of our knowledge, most of attempts to improve the thermal properties of PPC were performed on the PPC systems without residual catalysts. An important problem is that manufacture cost would be significantly enhanced if the catalysts was removed entirely from PPC resin. Therefore, it is very important to understand the specific properties of PPC modified by end-capping in the presence of residual catalysts in manufacture system, which will give a significant guidance in the mass limiting process of PPC. In our article, without further purification and removing residual catalyst, PPC was modified using 4, 4'-diphenylmethane diisocyanate (MDI) as an end-capping agent. The properties of the modified PPC were further systematically investigated using various characterizations, as well as the thermal degradation kinetics.

## EXPERIMENTAL

### Materials

PPC resin with content of carbon dioxide from 40%–42% was provided by Inner Mongolia Melic Sea High-Tech Group Company, China, number-average molecular weight is about 60,000–

150 000, and the melt flow rate 5–15 g/min, ashes is about 1%. PPC was used as received, without further purification and removing residual catalyst. If not specially defined, the word of “PPC” in this article is referred to PPC containing residual catalyst. Analytical pure MDI was purchased from Aladdin reagent in Shanghai.

### Preparation of PPC Modified with MDI

PPC was dried at 50°C for 24 h in a vacuum oven. Then the melt-blending of PPC and MDI was performed in internal mixer (LH60, Shanghai Kechuang Rubber and plastics equipment) with a screw speed of 40 r/min at 135°C and 170°C, respectively.

### Fourier Transform Infrared Spectroscopy (FTIR)

PPC+1%MDI blending sample was dissolved in acetone. Subsequently, the solution was filtrated by filter paper. At last, PPC were precipitated from the solution using methanol, and dried under vacuum at 50°C for 24 h. Neat PPC was also treated using the same procedure.

The measurement of infrared spectra was carried out using FTIR (Bruker 27). The dried specimens were dispersed into the KBr powder by mortar, and compressed to form disks.

### Melt Flow Index

The melt flow index (MFI) of PPC samples was measured according to ASTM D-1238 using a XNR-400B apparatus (De-Sheng Testing Equipment, China). The MFI measurements were carried out at 190°C under a load of 2.16 kg and the values are expressed in g/10 min.

### Gel Permeation Chromatography (GPC)

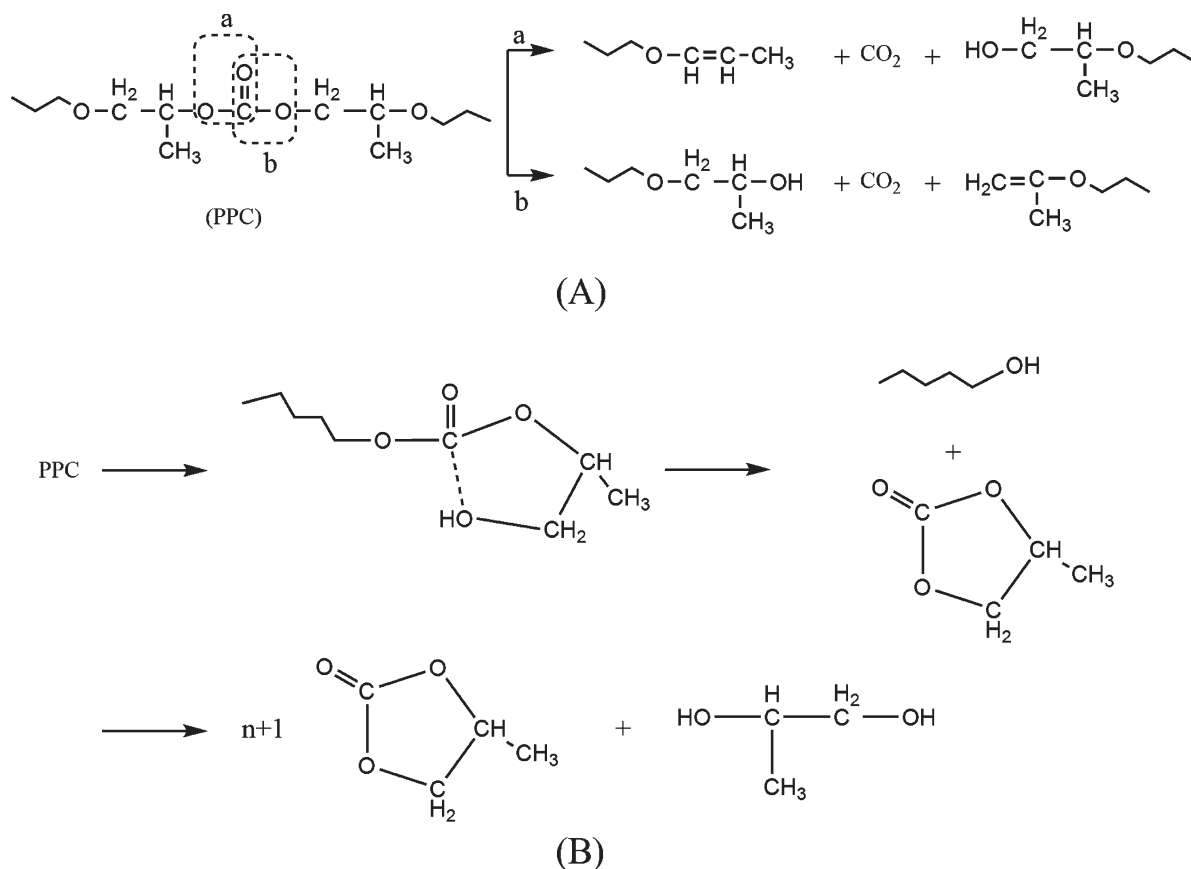
The average molecular weights and polydispersity index (PDI) were measured using a Waters 515 gel permeation chromatography system. Tetrahydrofuran (HPLC grade) was used as a solvent and an eluent at a flow rate of 2 mL/min. Number-average molecular weight ( $M_n$ ) and weight-average molecular weight ( $M_w$ ) were determined from calibration plots constructed with polystyrene standards. The dilute PPC solution was filtrated carefully to remove possible insoluble gel before it was injected into GPC column.

### Determination of the Gel Content

The gel content of the modified PPC was determined by a reported method.<sup>17</sup> Modified PPC sample (2 g) was suspended in 100 mL of chloroform at room temperature. The suspension was heated under continuous stirring until the boiling temperature of the solvent (62 °C), and refluxed for 1 h. The warm solution was then filtered to remove the soluble fraction, and the filter cake was washed with hot chloroform until the filtrate did not contain any polymer remainder. The residue was then washed with cold methanol and dried until constant weight. All samples were extracted using the same procedures.

### Thermogravimetric Analysis

Thermogravimetric analysis was performed with a TA Q600 instrument (TA instrument) from room temperature to 500°C, with a heating rate of 20°C/min under nitrogen protection.



**Figure 1.** Thermal degradation of PPC: Random chain scission (A); Unzipping degradation (B).

### Kinetics Degradation Study

According to the Friedman method,<sup>18</sup> as shown in eq. (1), the activation value can be calculated using the different thermogravimetric loss rate in differential curves of thermogravimetric analysis with various increasing rates of temperature.

$$\ln[(d\alpha/dT)] = \ln(A/\beta) + \ln f(\alpha) - E/(RT) \quad (1)$$

Here,  $f(\alpha)$  is a function of the conversion depending on the mechanism of the degradation reaction,  $\alpha$  the degree of conversion of the mass loss,  $A$  the pre-exponential factor,  $E$  the activation energy,  $T$  the absolute temperature, and  $R$  the gas constant. In particular, the function  $f(\alpha)$  is constant for a particular value of  $\alpha$ , the sum  $\ln(A/\beta) + \ln f(\alpha)$  is also constant. By plotting  $\ln[(d\alpha/dT)]$  against  $1/T$ , the value of the  $-E/R$  for a given value of  $\alpha$  can be directly obtained. Using this equation, it is possible to obtain values for  $E$  over a wide range of conversions.

### Scanning Electron Microscopy Analysis

The observation of the tensile fractured surfaces of composites was carried out on a Scanning Electron Microscope Philips XL-3 (FEI Company, Hillsboro, Oregon), operating at an acceleration voltage of 15 and 20 kV. The tensile fracture surfaces were vacuum coated with gold for scanning electron microscopy (SEM) observation.

### Tensile Testing

The tensile properties were measured with an Instron Model 5566 tensile tester (made in China), following the mounting

specification indicated by ASTM-D638. To ensure data accuracy and repeatability, multiple repeat tests were performed and average of a minimum of six valid values was used for the mechanical property analyses.

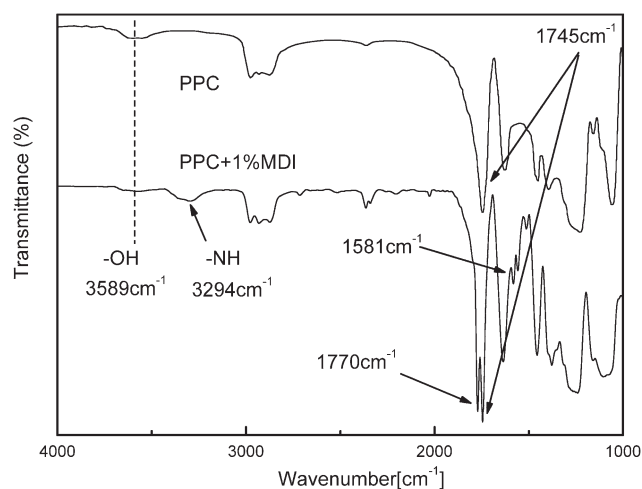
## RESULTS AND DISCUSSION

### Fourier Transform Infrared Spectroscopy

Figure 2 shows the Fourier transform infrared (FTIR) spectrum of neat PPC and PPC+1%MDI blend. The spectrum of neat PPC indicates a strong absorption near  $1745\text{ cm}^{-1}$ —characteristic of carbonate linkage. In addition, a weak absorption at  $3589\text{ cm}^{-1}$  is characteristic of end hydroxyl groups of PPC. When PPC was blended with MDI in molten state, end hydroxyl groups of PPC may react with MDI, leading to the formation of urethane linkages. In the spectrum of PPC+1%MDI blend, there are some new absorption peaks that are characteristic of urethane group. The peaks at  $3294\text{ cm}^{-1}$  and  $1770\text{ cm}^{-1}$  are due to  $\text{—N—H}$  and  $\text{—C=O}$  of urethane group, respectively. Moreover, the absorption at  $1581\text{ cm}^{-1}$  is assigned to benzene skeleton vibration. It is also found that the absorption peak intensity for end hydroxyl groups of PPC obviously decreased. According to the analysis of FTIR spectrum, it is confirmed that MDI can react with end hydroxyl groups of PPC in molten state.

### Effect of MDI on the Macromolecular Structure of PPC

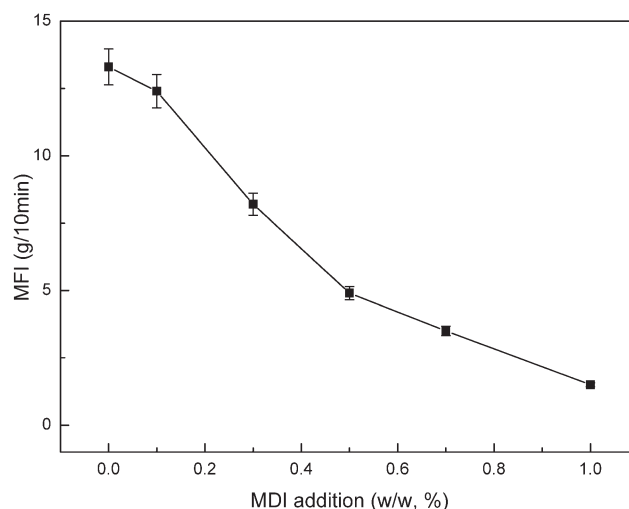
MDI is a basic compound in urethane chemistry giving a large variety of reactions. In melt blending, its bifunctionality could



**Figure 2.** FTIR spectrum of neat PPC and PPC+1%MDI blending sample.

cause not only end-capping reaction, but also chain-extension, even crosslinking reaction on PPC. MFI, GPC, and gel content measurements were carried out to characterize the effect of amount of MDI on the macromolecular structure of PPC.

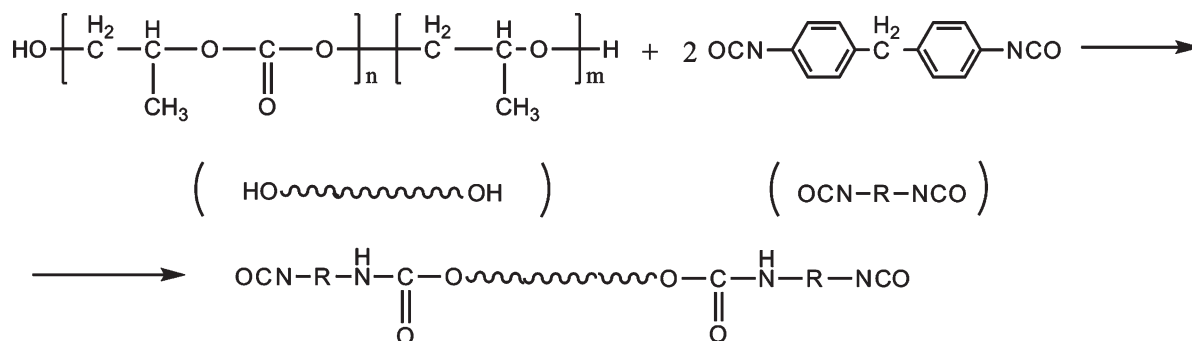
Figure 3 shows the effect of the amount of MDI on MFI of PPC. For neat PPC, a typical value of 13.3 g/10 min was obtained. When 0.1% MDI was added, the MFI value kept almost unchanged. However, an obvious decrease in MFI was observed when the amount of MDI exceeded to 0.3%. When MDI addition was increased to 1.0%, the MFI decreased to 1.5 g/10 min. It is well known that MFI value of polymer will decrease when its molecular weight or gel content increases.



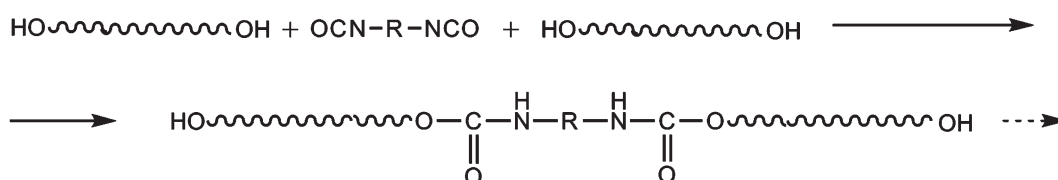
**Figure 3.** Effect of the amount of MDI on MFI of PPC samples.

Low value of MFI, meaning a high viscosity in the melt for modified PPC, could be due to the occurrence of a chain extending reaction, and even forming of a mild crosslinking structure. Figure 4 presents the proposed end-capping reaction and chain-extension reaction of PPC by MDI.

GPC measurement can provide information about molecular weight of linear macromolecule, which can serve as a parameter to evaluate the macromolecular structure and thermal stability of PPC at the elevating temperature during the manufacture process. The number-average molecular weight ( $M_n$ ), weight-average molecular weight ( $M_w$ ) and PDI were determined by GPC measurement. Before the dilute PPC solution was injected into



**(A) end-capping reaction of PPC by MDI**



**(B) chain-extension reaction of PPC by MDI**

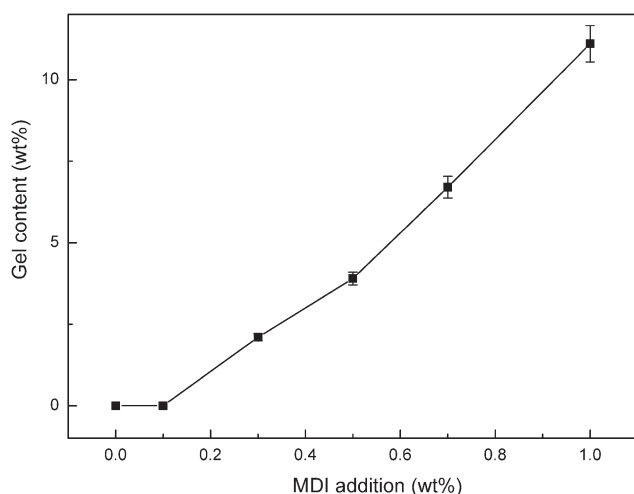
**Figure 4.** Proposed end-capping reaction and chain-extension reaction of PPC by MDI.

**Table I.** GPC Data of Neat PPC and PPC Blended with Various Amount of MDI at 135°C for 5 min

	$M_n \times 10^3$ g/mol	$M_w \times 10^3$ g/mol	PDI
Neat PPC (unheated)	71	196	2.76
Neat PPC (135°C, blending 5 min)	50	143	2.86
PPC+0.1%MDI (135°C, blending 5 min)	62	180	2.90
PPC+0.5%MDI (135°C, blending 5 min)	131	172	1.31
PPC+1.0%MDI(135°C, blending 5 min)	131	187	1.43

GPC column, it was filtrated carefully to remove possible insoluble gel. From Table I, it was found that both  $M_n$  and  $M_w$  for neat PPC significantly decreased after heated at 135°C for 5 min. When 0.1% of MDI was used to blend with neat PPC for 5 min, the value of  $M_n$  only displayed a slight decreased compared to the neat PPC resin. With the amount of MDI increasing, the value of  $M_n$  increased obviously. For example,  $M_n$  of neat PPC(unheated) and PPC blended with 1.0% MDI at 135°C for 5 min were  $71 \times 10^3$  g/mol and  $131 \times 10^3$  g/mol, respectively. The increase in  $M_n$  was up to 84%. As expected, when the amount of MDI increased, the polydispersity of modified PPC showed a trend to decrease. A similar result was reported by Gun<sup>19</sup> when *N, N'*-dinitrosopentamethylene tetramine was used as blowing and chain-extension agent for PPC.

Figure 5 shows the effect of the amount of MDI on gel content of the modified PPC samples. It can be seen that the gel content for neat PPC and PPC+0.1% MDI samples were zero. With increasing amount of MDI, the gel content increased obviously. When 1.0% MDI was added, the modified PPC showed a gel content of 11.1%.



**Figure 5.** Effect of the amount of MDI on gel content of modified PPC samples.

From the analysis of MFI, GPC, and gel content measurements, it can be proposed that mainly end-capping reaction occurring on PPC chain when 0.1% MDI was added. When the amount of MDI exceeded to 0.3%,  $M_n$  and gel content for the modified PPC samples started to increase obviously, and MFI decreased largely. It is due to the fact that chain-extension and crosslinking reactions were carried out between PPC and MDI in addition to the end-capping reaction. It is obvious that all the reactions, including end-capping, chain-extension, and crosslinking, are positive to improve the thermal stability of PPC.

To further confirm the end-capping reaction of PPC modified with 0.1% MDI, GPC characterization of the PPC+MDI blend was performed at different processing temperatures and time. Table II presents GPC data for neat PPC and PPC+0.1% MDI samples with different processing time at 135°C. As shown in Table II, both  $M_n$  and  $M_w$  of neat PPC decreased obviously when neat PPC was heated for 5 min. With heating time up to 10 min,  $M_n$  and  $M_w$  of neat PPC became much lower. However, when 0.1% of MDI was utilized to blend with neat PPC for 5 min, the value of  $M_n$  displayed a slight decreased compared to that of neat PPC resin. Even when the heating time was up to 10 min, the value of  $M_n$  still kept almost unchanged comparing to that of neat PPC resin. Therefore, the addition of MDI had a good effect to inhibit the thermal degradation of PPC. It can be explained by that MDI brought about an end-capping reaction with hydroxyl group of PPC and prevented the unzipping degradation resulted from the hydroxyl group. However,  $M_w$  of modified PPC showed a certain decreasing. It can be explained by that the terminal hydroxyl groups in PPC chains with higher molecular weight were less active to react with MDI as compared to that of PPC chains with lower molecular weight, which greatly increased the possibility of thermal degradation of PPC chains with higher molecular weight. As a result, the value of  $M_w$  decreased.

For comparison, the blending of MDI and PPC was performed at 170°C. As shown in Table III, the molecular weight ( $M_n$ ,  $M_w$ ) of neat PPC blended at 170°C became much lower than that of PPC blended at 135°C. When the blending of PPC and 0.1% MDI was carried out at 170°C for 5 min, the  $M_n$  of PPC was little higher than that of neat PPC, with a slight decrease of the

**Table II.** GPC Data of neat PPC and PPC+0.1%MDI sample with different processing time at 135°C

	$M_n \times 10^3$ g/mol	$M_w \times 10^3$ g/mol	PDI
Neat PPC (unheated)	71	196	2.76
Neat PPC (135°C, blending 5 min)	50	143	2.86
Neat PPC (135°C, blending 10 min)	38	119	3.13
PPC+0.1%MDI (135°C, blending 5 min)	62	180	2.90
PPC+0.1%MDI (135°C, blending 10 min)	73	172	2.36

**Table III.** GPC Data of Neat PPC and PPC+0.1%MDI Sample with Different Processing Temperatures

	$M_n \times 10^3$ g/mol	$M_w \times 10^3$ g/mol	PDI
Neat PPC (unheated)	71	196	2.76
Neat PPC (170°C, blending 5 min)	32	102	3.19
PPC+0.1%MDI (135°C, blending 5 min)	62	180	2.90
PPC+0.1%MDI (170°C, blending 5 min)	74	166	2.24

$M_w$ . Thus, a small amount of MDI (0.1%) can prevent the unzipping degradation and increase the thermal stability of PPC, which significantly enhance the manufacture temperature and processing time for PPC and increase the application potential.

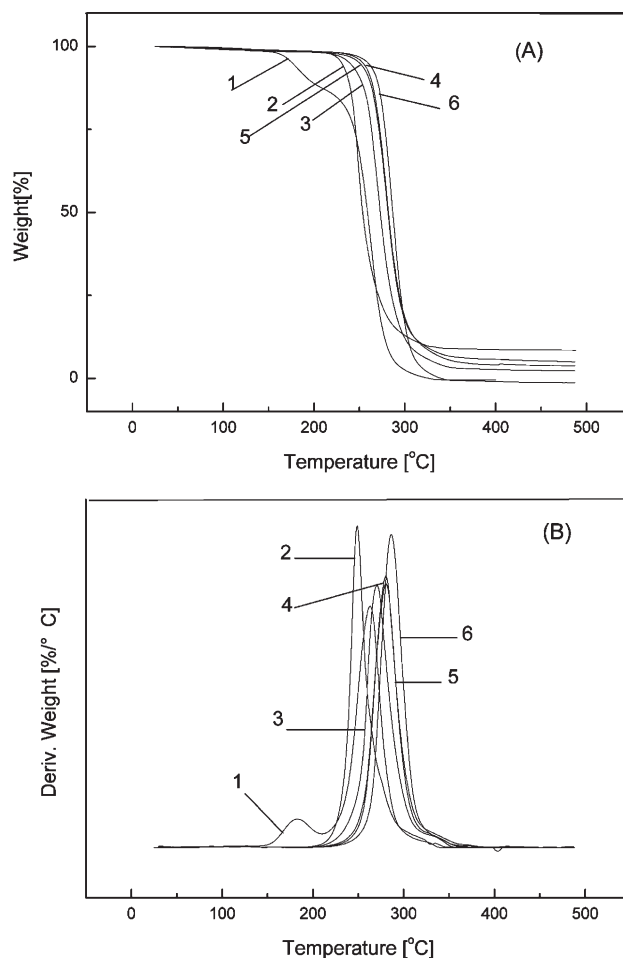
#### Effect of MDI on the Thermal Stability of PPC

Removing the residual catalyst thoroughly from the PPC resin will largely improve the thermal stability of PPC. However, the cost for the deep purification was too high for PPC mass production. Before exploiting more efficient and low-cost purification system, it is very important to study the specific properties of PPC modified using end-capping agents in the presence of residual catalysts.

In order to investigate the effect of amount of MDI on the thermal stability of PPC containing residual catalysts, PPC+MDI blends with different mixing ratio were analyzed using the thermogravimetric analysis (TGA). Figure 6 shows TGA and differential thermal analysis (DTG) of neat PPC and PPC+MDI blends with different mixing ratio. The TGA analysis data was summarized in Table IV.

From Figure 6, it can be seen that the degradation of the modified PPC took place at higher temperature than that of neat PPC. With the increase of MDI content, the thermal degradation temperature shifted to a higher temperature, as listed in Table IV. Here,  $T_{-5\%}$ , the temperature at 5% weight loss, represents the onset temperature of thermal degradation, while  $T_{-50\%}$ , the temperature at 50% weight loss, is the temperature regarded as the midpoint of the degradation process. The peak temperatures ( $T_{max}$ ) in DTG curves is the temperature at which the mass loss rate is the fastest. It can be found that  $T_{-5\%}$  and  $T_{-50\%}$  of neat PPC were 176.3°C and 258.5°C, respectively. With 0.1% of MDI addition,  $T_{-5\%}$  and  $T_{-50\%}$  of the modified PPC increased to 233.0°C and 253.3°C, respectively. When the amount of MDI was 1%, the  $T_{-5\%}$  reached up to 259.6°C from 176.3°C, and the  $T_{-50\%}$  was up to 286.0°C from 258.5°C for neat PPC.

For summarization,  $T_{max}$  of the DTG curves are listed in Table IV. It can be seen that  $T_{max}$  of the modified PPC were higher than that of neat PPC. Interestingly, the DTG curve of neat PPC exhibited two peaks, which was different from those of modified PPC (only one peak on the DTG curves). One peak temperature was at about 184.0°C, which was much lower than

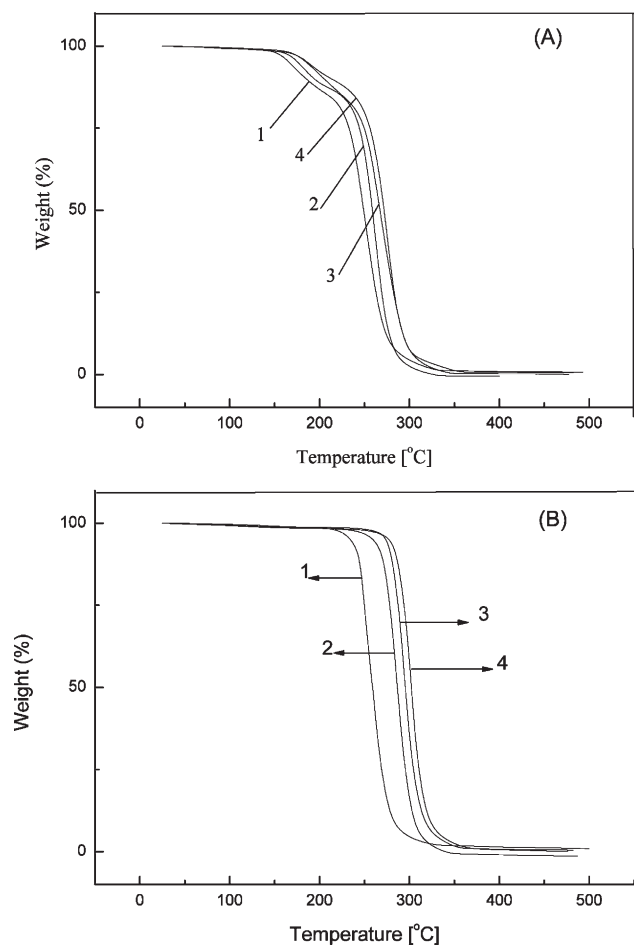
**Figure 6.** TGA (A) and DTG (B) curves of PPC+MDI blends at the heating rate of 20°C·min<sup>-1</sup> (1: neat PPC; 2: PPC+0.1%MDI; 3: PPC+0.3%MDI; 4: PPC+0.5%MDI; 5: PPC+0.7%MDI; 6: PPC+1%MDI).

the degradation temperatures of the modified PPC. Another peak temperature was at about 263.6°C, which was similar to  $T_{max}$  of the modified PPC. This implies that different mechanisms functions during the whole degradation process of neat PPC and the modified PPC.

Based on the TGA and DTG curves, it is speculated that neat PPC would decompose with a mechanism of the unzipping degradation in a low temperature range, while it would occur a

**Table IV.** TGA Data of PPC+MDI Blends at the Heating Rate of 20°C·min<sup>-1</sup>

Composite PPC	$T_{-5\%}$ (°C)	$T_{-50\%}$ (°C)	$T_{max}$ (°C)
Neat PPC	176.3	258.5	184.0, 263.6
PPC+0.1%MDI	233.0	253.3	248.4
PPC+0.3%MDI	239.1	272.8	270.5
PPC+0.5%MDI	254.6	281.8	280.6
PPC+0.7%MDI	250.2	281.6	280.0
PPC+1%MDI	259.6	286.7	285.6



**Figure 7.** TGA curves of neat PPC (A), PPC+1%MDI (B) samples at various heating rates (1: 10°C/min; 2: 20°C/min; 3: 30°C/min; 4: 40°C/min).

random chain scission in a high temperature range. The similar result was also found by the researches of Kuran<sup>9</sup> and Liu<sup>10</sup>. They confirmed that the temperature for unzipping degradation was lower than that of the random chain scission. In the presence of catalysts, the unzipping degradation of PPC is further accelerated at low temperature. In chain unzipping degradation, neat PPC would form a five-member cycle ending via the hydroxyl groups. And then, PPC will carry out a random chain scission with increasing temperature.

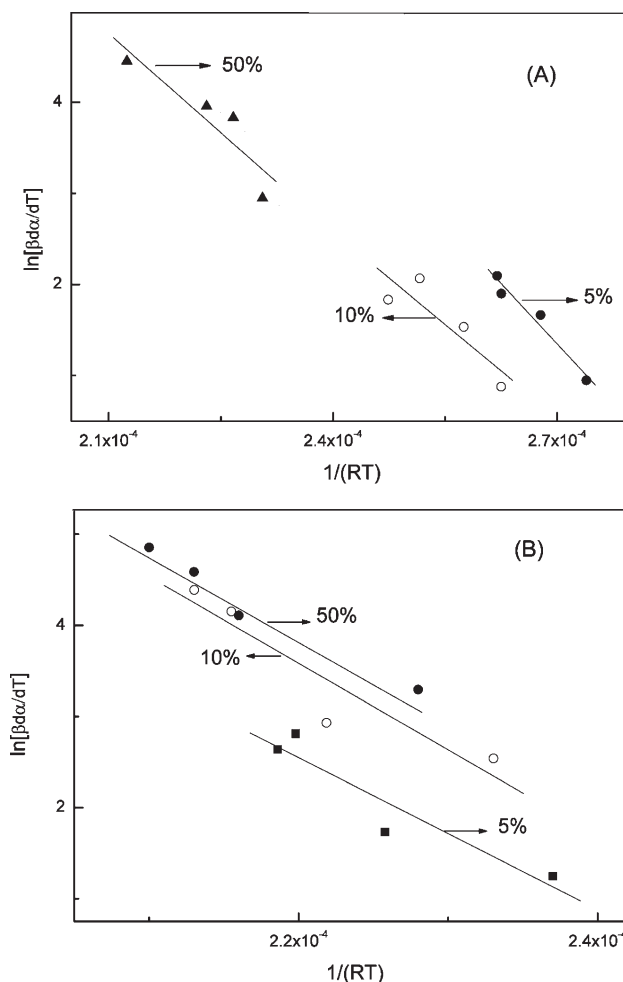
Combined with the analysis of MFI, GPC, and gel content measurements, it can be pointed out that an end-capping reaction occurred on PPC chains when 0.1% MDI was added. The terminal hydroxyl groups of PPC were protected by end-capping and initial chain unzipping from the terminal hydroxyl groups was inhibited. As a result, the unzipping degradation of PPC at low temperatures was prevented, which resulted in only one weight loss for the modified PPC and an improvement on thermal stability of PPC. However, when the amount of MDI exceeded to 0.3%, there was not only end-capping reaction, but also chain-extension and crosslinking reaction occurring on PPC chains. With increasing the amount of MDI, the thermal stability of PPC was further enhanced. It can be attributed to the increase in molecular weight and gel content of the modi-

fied PPC, which reduced the amount of active terminal groups and further restricts unzipping to some extent.

According to the discussions, we conclude that the initial chain unzipping from the terminal hydroxyl groups can be inhibited by using MDI as a modified agent even in the presence of residual catalyst. Thus the thermal stability of PPC is significantly enhanced.

### Thermal Degradation Kinetics of Neat PPC and PPC+1%MDI Blend

The properties of thermal degradation of neat PPC and PPC+MDI blend are crucial to develop PPC with predicted thermal stability and guide the manufacture process. In this study, the Friedman method was applied to analyze the thermal degradation kinetics of PPC. As results shown in Figure 7, neat PPC and PPC+1%MDI were characterized by TGA at the heating rates of 10°C/min, 20°C/min, 30°C/min, 40°C/min under nitrogen protection, respectively. It was found that the two samples had a similar degradation tendency at different heating rates. The samples had a higher degradation temperature with increasing heating rates. This can be explained by the fact that the degradation of polymers is regarded as a molecular chain



**Figure 8.** Plots of  $\ln[\beta dz/dT]$  as a function of  $1/(RT)$  for neat PPC (A) and PPC+1%MDI blends (B) with Friedman method.

**Table V.** Values of  $k$ ,  $r$  and  $E_a$  from Friedman equation for neat PPC and PPC+1%MDI blends

Conversion ( $\alpha$ )	Neat PPC		PPC+1% MDI	
	$R$	$E$ (KJ/mol)	$r$	$E$ (KJ/mol)
5%	0.98	88.3	0.94	83.4
10%	0.88	68.0	0.94	95.0
50%	0.90	72.5	0.99	92.9

segment movement. The degradation was delayed because molecule movement can not follow when the temperature was increased.

The degradation kinetics was obtained according to the Friedman method (Figure 8). From the linear correlation coefficient ( $r$ ) listed in Table V, the  $r$  values were almost higher than 0.96, which indicates the Friedman method is fit for the thermal degradation kinetics of neat PPC and PPC+MDI blend. The activation energies for two samples with different conversions were calculated according to the slopes in the Friedman equation. The PPC+1%MDI blend had higher activation energy than neat PPC in the degradation process with different weight loss rates, which demonstrates that the thermal stability of PPC was significantly improved when it was modified with MDI. Furthermore, neat PPC and PPC+1% MDI had different tendencies in the degradation activation energy. The degradation activation energy values of neat PPC remarkably decreased at first, and then slightly increased with the increasing weight loss rates. However, the degradation activation energy values of PPC+1% MDI displayed a slight increase. These differences demonstrate that neat PPC and PPC+1% MDI possibly have different degradation mechanisms. It can be attributed to that, with the end-capping role of MDI, the unzipping degradation of PPC at low temperature is effectively prevented.

### Tensile Properties of PPC+MDI Blends

As the results shown in Figure 9, the tensile strength of PPC was markedly enhanced with the increasing amount of MDI. When MDI of 1.0% was added, the tensile strength increased up to 12.8 MPa from the original 4.74 MPa for neat PPC. The notable enhancement in tensile strength is due to the increasing molecular weight and gel content of the modified PPC with the increasing amount of MDI.

In addition, the morphology of the modified PPC was observed by SEM. Figure 10(A) shows the tensile fracture of neat PPC that is very smooth and homogeneous. It can be due to the fact that the deformation can be recovered quickly because PPC has a high elasticity at room temperature. Interestingly, SEM pictures for the tensile fracture surfaces of PPC+MDI blends shown in Figure 10 display many outstanding white color bright spots. A reasonable explain is followed as: when MDI content increased, the crosslinking degree of PPC increased. In the PPC melt, the crosslinked part had higher viscosity and stronger polarity which resulted in an aggregation of crosslinked PPC. At last, the phase of rich crosslinked PPC formed in PPC matrix, and the phase separation took place. And these white color

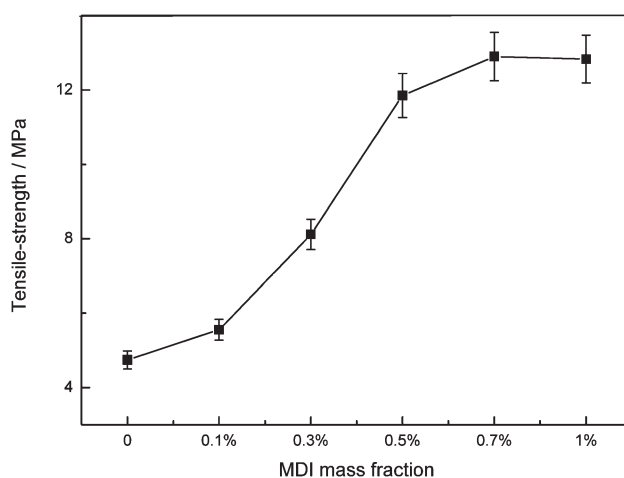
bright spots should be the dispersion phases. These dispersion phases had higher modulus that resulted in an increase in the tensile strength. Specifically, the nonreversible deformation point of PPC+0.5% MDI can also be detected clearly when the SEM picture of tensile fracture was amplified up to 10,000 time [Figure 10(E)]. With the increasing amount of MDI, more and more white spots appeared which resulted in an obvious increase in the tensile strength of PPC.

Of course, we can not exclude the possibility that these bright spots caused by locally enrichment of MDI and its reaction products which can accumulate charges.

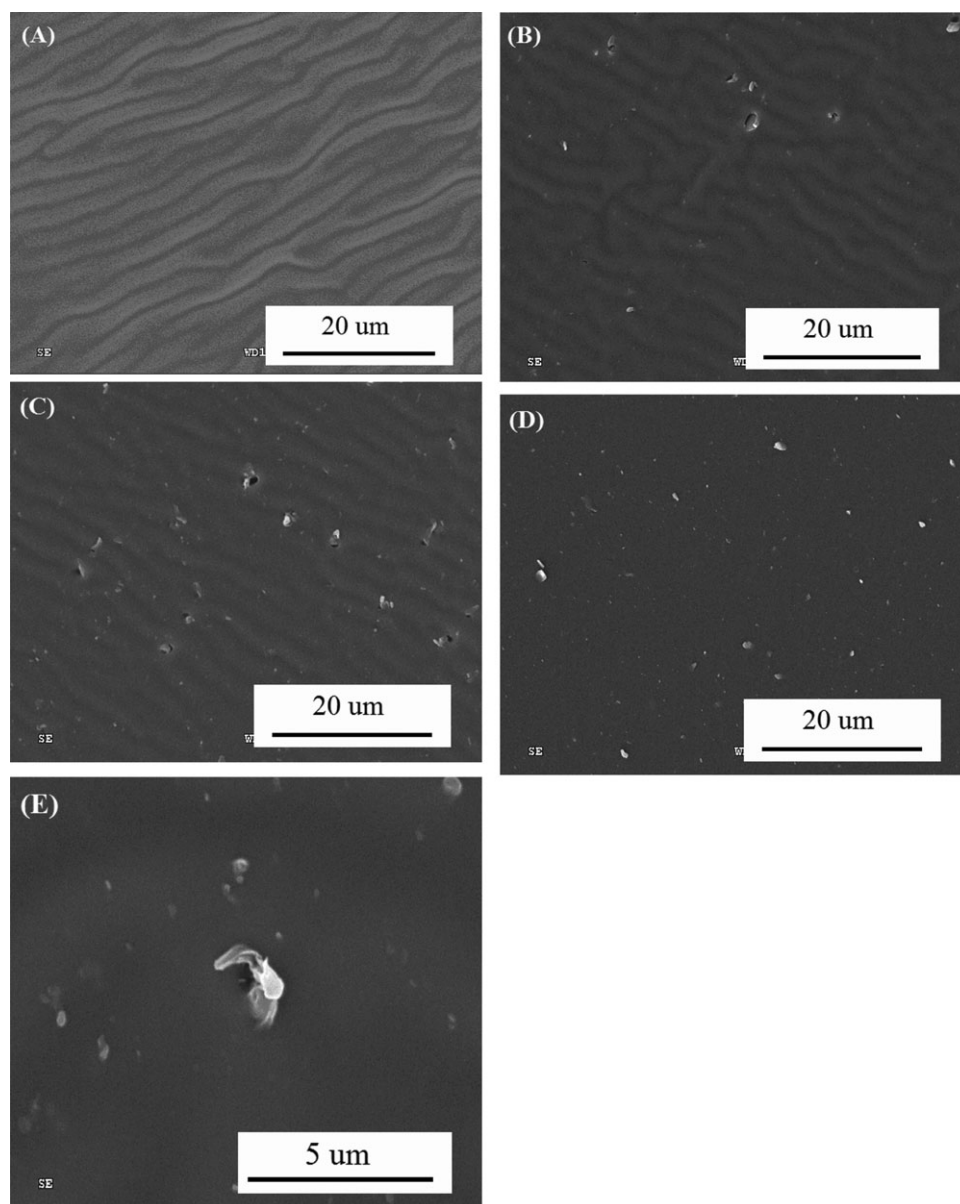
### CONCLUSION

The modified PPC was prepared by using melt blending neat PPC with MDI as an end-capping agent. MFI, GPC, and gel content measurements showed that mainly end-capping reaction occurred on PPC chains when 0.1% of MDI was added. However, as the amount of MDI exceeded to 0.3%, end-capping, chain-extension, and crosslinking reactions were synchronously carried out on PPC.

According to TGA results, it is found that the presence of residual catalyst could accelerate the unzipping reaction of neat PPC with terminal hydroxyl groups and induce the reaction below 200°C. When the terminal hydroxyl groups were end-capped by MDI, the unzipping degradation in the lower temperature range was inhibited effectively, even without removing the residual catalyst. The random scission degradation at higher temperatures shifted to a higher temperature as well. With 0.1% of MDI,  $T_{-5\%}$  and  $T_{-50\%}$  of the end-capped PPC increased to 233.0°C and 253.3°C, respectively. With the increasing amount of MDI, the thermal stability of PPC was enhanced obviously thanks to the increase in molecular weight and gel content of the modified PPC caused by the chain-extension and crosslinking reactions. When the amount of MDI was 1%, the  $T_{-5\%}$  reached 259.6°C from 176.3°C for neat PPC, and the  $T_{-50\%}$  was 286.0°C from 258.5°C for neat PPC. It indicates that MDI can

**Figure 9.** Effect of MDI content on tensile property of PPC+MDI blending samples.





**Figure 10.** SEM of fractured surface of neat PPC and PPC+MDI blending ((A) neat PPC (2000X); (B) PPC+0.1% MDI (2000X); (C) PPC+0.5% MDI (2000X); (D) PPC+1% MDI (2000X); (E) PPC+0.5% MDI (10,000X)).

prohibit the unzipping degradation and enhance the thermal stability of PPC even in the presence of residual catalyst.

The tensile properties of PPC can be largely enhanced with increasing amount of MDI. When 1.0% of MDI was added, the tensile strength increased up to 12.8 MPa from the original 4.74 MPa for neat PPC. It is proposed that the molecular weight and gel content increased with increasing amount of MDI, which greatly enhanced the tensile strength of PPC.

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