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## **ARTICLE TYPE**

# A novel method to improve the thermal stability of Poly (propylene carbonate)

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In the present work, the surfactant, phosphoric ester of poly (ethylene oxide) (10) nonyl phenyl (abbreviated as NP-10P in the following), was incorporated into poly (propylene carbonate) (PPC) by melt-blending. Characterization data by TGA and Py-GC/MS have suggested that the obtained PPC/NP-10P complex displays excellent thermal stability as compared to pure PPC. The thermal decomposition temperature with 5% loss in weight increases about 103 °C for 180 °C for PPC to 283 °C of PPC with 15wt% NP-10P.

<sup>10</sup> In particular, with only 1 wt% of NP-10P incorporated into the PPC, about 74 °C increase in decomposition temperature is found. And the pyrolysis mechanism of PPC used before and after modification by NP-10P varies from chain unzipping degradation to chain random scission followed by the unzipping degradation. The results of <sup>31</sup>P NMR, FTIR and Intrinsic viscosity measurement have illustrated that the PPC is end-capped with NP-10P, which leads to the improvement of thermal stability and the change in pyrolysis mechanism of PPC. Moreover, this new finding will facilitate development and massive applications of this biodegradable material.

#### 15 Introduction

Poly (propylene carbonate) (PPC), which is an alternative copolymer consisted of propylene oxide (PO) and carbon dioxide (CO<sub>2</sub>), has attracted extensive attention not only for its high value-added fixation of CO<sub>2</sub>, but also for its biodegradability and <sup>20</sup> biocompatibility <sup>1, 2</sup>. It has been used in various areas such as biomedical materials, plasticizer for rubber or thermoplastics, surfactants, packaging materials, *etc* <sup>3-6</sup>. However, the weak carbonate linkage in the backbone and reactive end groups of PPC lead to its relatively low thermal decomposition temperature <sup>25</sup> (the onset of decomposition in the range of 150~180 °C that is

<sup>25</sup> (the onset of decomposition in fange of 150-160° C that is unfavourable for processing) <sup>2, 7-10</sup>. Generally, most polymers or the blending of the resins are performed at temperature high up to 150 °C with melting time over 5 min in the manufacturing process. Under such a rigorous condition PPC would be degraded <sup>30</sup> obviously and a poor blending was inevitable. Therefore, it is of great necessity to improve the thermal stability of PPC for

practical applications. According to the reported references, the backbone structure plays a great role in thermal decomposition of PPC. Inoue *et al.*<sup>7-</sup> <sup>35</sup> <sup>10</sup> have indicated that the thermal decomposition of PPC exhibits two decomposition mechanisms: the main chain random scission (Scheme 1) and unzipping degradation (Scheme 2). The reactive hydroxyl end group in PPC can lead to a chain unzipping degradation mechanism originating from a "backbiting" <sup>40</sup> attacking of terminal hydroxyl groups on the carbonyl group. So the PPC with uncapped end group or with lower molecular weight more easily induces chain unzipping reaction due to the existence of abundance of hydroxyl group. In contrast, PPC with very high molecular weight mainly induces the main chain <sup>45</sup> random scission reaction due to a small amount of the active terminal group, which has higher thermal stability than those PPC with original very low molecular weight in which the decomposition mechanism is controlled by chain unzipping degradation.

$$\bigcirc -CH_2CH \bigcirc O-CH_2O - CH_2O \\ CH_3 & CH_3 & CH_3 & (PPC) \\ \hline$$

main chain 🚽 random scission

 $CO_2$  +  $HO-CH-CH_2O$ 

Scheme 1 The degradation of PPC: Random chain scission.

O-CH=CH-CH<sub>3</sub>



**Scheme 2** The degradation of PPC: Unzipping degradation. Then thus the terminal hydroxyl group of PPC is a key factor

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affecting the unzipping degradation of PPC. The thermal stability of PPC can be enhanced mainly via the end-capping of hydroxyl groups, hydrogen bonding interaction introduced into blends, or chain-extension and cross linking reactions between PPC and <sup>5</sup> other components <sup>11-17</sup>. Tao *et al.* <sup>11</sup> have prepared UVcrosslinkable PPC by the terpolymerization of CO<sub>2</sub>, propylene oxide, and allyl glycidyl ether. The crosslinked PPC showed

- improvement (the onset degradation temperature increased by 26  $^{\circ}C \sim 47 ^{\circ}C$ ) in thermal stability in comparison with pure PPC. Its <sup>10</sup> preparation process, however, was very complicated. Peng *et al.*
- <sup>12</sup> reported a method to modify PPC by casting from solution with some agents, such as maleic anhydride (MA), benzoyl chloride, ethyl silicate, phosphoryl chloride, and so on; due to the endcapping reaction, the thermal stability of PPC was enhanced (5%)
- <sup>15</sup> weight loss temperature increased by 27 °C ~ 42 °C). Furthermore, Lai *et al.* <sup>13</sup> and Xiong *et al.* <sup>14</sup> found that MA and its macrocycle radical copolymers could enhance the thermal stability of PPC. Meanwhile, MA brought about intercoupling in macromolecules, and an increase in molecular weight of PPC, resulting in
- <sup>20</sup> enhancement of the thermal stability of PPC. Additionally, Yu *et al.* <sup>15, 16</sup> have blended PPC with organic compounds like octadecanoic acid (OA) and metal octadecanoic acid salt by casting from solution, and the thermal stability was noted to have been improved by hydrogen bonding interaction between
- <sup>25</sup> components. In particular, the 5% weight loss temperature with 1 wt% organic compounds increased by 38 °C and 14 °C, respectively. In the modification way mentioned above, however, there was limited improvement for the thermal stability of PPC especially when adding a small amount of agents or organic
- <sup>30</sup> compounds. In addition, most of the above attempts were via casting from solution. Generally, the melt-blending method, which is easy and convenient, is more suitable in the process of manufacture.

Pang *et al.* <sup>17</sup> have blended PPC with 4, 4'-diphenylmethane <sup>35</sup> diisocyanate (MDI) through melt compounding. When 0.1% of MDI was added,  $T_{5\%}$  of PPC/MDI composite was increased by 57 °C while  $T_{50\%}$  and  $T_{max}$  of composite almost were not enhanced, in which the end-capping reaction was mainly carried out on PPC

- chains. As the amount of MDI exceeded to 0.3%, end-capping, <sup>40</sup> chain-extension, and cross linking reactions occurring between PPC and MDI could effectively improve the thermal stability ( $T_{5\%}$  and  $T_{50\%}$  of PPC/1wt% MDI blend increased to 259.6 °C and 286.7 °C respectively, which were about 83 °C and 28 °C higher than that of pure PPC). Nevertheless, it leaded to a high
- <sup>45</sup> viscosity in the melt that was unfavourable for manufacture. Therefore, we aim to prepare the thermostable PPC by melt blending in which the preparation method is simple and in which this biodegradable material can be massive applications. Phosphoric ester of poly (ethylene oxide) (10) nonyl phenyl
- <sup>50</sup> (abbreviated as NP-10P in the following) (Scheme 3) possesses an abundant of terminal hydroxyl groups. It should be capable of forming hydrogen bonding with carbonate groups in PPC or endcapping with PPC. Moreover, it may be chain extender for PPC because some references have been reported that phosphate can <sup>55</sup> be used as chain extender for PET <sup>18-20</sup>. All theses interactions

can improve the thermal stability of PPC. In the present work, we report a novel method to improve the thermal stability of PPC by melt blending with NP-10P. The thermal stability and decomposition behaviour of PPC/NP-10P 60 complex are investigated by TGA and Py-GC/MS measurements and the interactions between PPC and NP-10P are also discussed by <sup>31</sup>P NMR, FTIR and Intrinsic viscosity measurements.



Scheme 3 Chemical structures of PPC and NP-10P.

#### 65 Experimental

#### Materials

Totally biodegradable poly (propylene carbonate) (PPC) was supplied by Mengxi High-tech Materials Company (Inner Mongolia). The weight-average molecular weight and the 70 polydispersity index of PPC determined by gel permeation chromatography (GPC) were  $2.7 \times 10^4$  and 1.99, respectively. Phosphoric ester of poly (ethylene oxide) (10) nonyl phenyl was purchased from Tokyo Chemical Industry (Shang Hai) Co., Ltd and used as received. Other reagents were all commercially 75 available and refined according to the standard procedures.

#### **Preparation of PPC/NP-10P complex**

PPC was melt-blended with NP-10P in weight proportions ranging from 1 wt% to 15 wt%. Prior to blending, PPC and NP-10P were dried in vacuum at 50 °C for 24 h. The mixing was <sup>80</sup> practiced at a rotating speed of 50 rpm at 140 °C for 5 min on a Haake batch-intensive mixer (Haake Rheomix 600, Germany) with a batch volume of 55 ml. The pure PPC was subjected to the same treatment for comparison of thermal history.

#### Characterizations

#### 85 Thermogravimetric analysis (TGA) measurement

Thermal properties of NP-10P, PPC and PPC/NP-10P complex were evaluated by thermogravimetric analysis (TGA). The thermal degradation process was recorded with a Perkin–Elmer Pyris 1 TGA thermal analyzer. The samples under a nitrogen <sup>90</sup> protective atmosphere were heated from 50 to 500 °C at a rate of 20 °C min<sup>-1</sup>.

#### **Py-GC/MS** measurement

The decomposition behaviour of PPC and PPC/NP-10P analyzed with the Pyrolysis gas complex was 95 chromatography/mass spectrometer (Py-GC/MS) (SHIMADZU GCMS-QP5050A equipped with PYR 4A pyrolyzer). The samples were heated at 230, 310 and 380 °C respectively for 1 min. The pyrolysed products were carried through the fused silica capillary column by the helium carrier gas and separated at the 100 same time, and then detected by the MS detector. Data analyses were performed on an HP Chem Station Wiley 275 (version 4.00) via matching the NIST Mass Spectra Library by comparison.

#### <sup>31</sup>P NMR measurement

The <sup>31</sup>P NMR spectra were recorded on a Bruker Model <sup>105</sup> Advance DMX 300 operating at 25 °C and 162 MHz for <sup>31</sup>P. The spectra were acquired with 16K points, a recycle delay of 5 s, a scan number of 5000, an acquisition time of 25 ms, and <sup>31</sup>P 90° pulse. The <sup>31</sup>P 90° pulse length was 16 µs with an attenuation level of 3.3 dB. The chemical shifts were referenced internally to Polymer Chemistry Accepted Manuscript

the resonance of 85% orthophosphoric acid at 0 ppm for the  ${}^{31}P$  NMR spectrum.

#### FTIR measurement

- Fourier transform infrared spectroscopy (FTIR) spectra were s recorded by using of a Tensor-27 (Bruker) spectrometer at a resolution of 2 cm<sup>-1</sup> and 32 scans were signal-averaged. The testing range was from 400 to 4000 cm<sup>-1</sup>. The samples were prepared in 2.0% (w v<sup>-1</sup>) chloroform solutions. Then the solutions were cast into films on KBr crystal. Most of the solvent was
- <sup>10</sup> evaporated at room temperature. For further removal of the residual solvent, all the samples were dried under vacuum at 80 °C until constant weight. Finally put them in the vacuum desiccators before testing.

#### Intrinsic viscosity measurement

Intrinsic viscosity [ $\eta$ ] measurements were carried out in THF at 298  $\pm$  0.1 K using an Ubbelohde suspended level capillary viscometer. The intrinsic viscosities were obtained from the intercept of the plot of viscosity number against concentration.

#### **Results and discussion**

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#### 20 Thermal stability of PPC/NP-10P complex



Figure. 1 Thermal stability of PPC/NP-10P complex, PPC and NP-10P.

Table 1 Thermal	degradation	data	of PPC/NP	-10P	complex,	PPC
and NP-10P.						

sample	T <sub>5%</sub>	T <sub>50%</sub>	T <sub>max</sub>
PPC	180.6	229.3	228.8
PPC/1wt% NP-10P	254.0	295.4	297.7
PPC/5wt% NP-10P	258.2	299.4	300.1
PPC/10wt% NP-10P	277.4	310.4	312.4
PPC/15wt% NP-10P	283.0	312.9	310.7
NP-10P	277.7	330.0	338.7

As shown in Figure 1, it can be found the degradation took place at higher temperature in the PPC/NP-10P complex than in neat PPC. With increasing the content of NP-10P, the thermal degradation temperature shifted to a higher temperature, as listed <sup>30</sup> in Table 1. It can be seen that  $T_{5\%}$ ,  $T_{50\%}$  and  $T_{max}$  of pure PPC are 180.6 °C, 229.3 °C and 228.8 °C, respectively. With the addition of 1wt% NP-10P,  $T_{5\%}$ ,  $T_{50\%}$  and  $T_{max}$  of PPC/NP-10P complex increase to 254.0 °C, 295.4 °C and 297.7 °C respectively, which are about 74 °C higher than that of pure PPC. With increasing the <sup>35</sup> addition of NP-10P, the thermal stability of PPC/NP-10P

complex is gradually enhanced. When the amount of NP-10P is 15wt%,  $T_{5\%}$ ,  $T_{50\%}$  and  $T_{max}$  reach up to 283 °C, 312.9 °C and 310.7 °C respectively, all of which are approximately 100 °C higher than those of pure PPC. As compared to the complexes of <sup>40</sup> PPC with organic compounds such as MA or OA *etc* <sup>11-17</sup>, the PPC/NP-10P complex has much better thermal stability:  $T_{5\%}$  of the PPC/NP-10P complex reaches to 254~283 °C, while those of the references have been reported are less than 260 °C; both  $T_{50\%}$  and  $T_{max}$  of the PPC/NP-10P complex are higher or close to <sup>45</sup> 300°C, while those of the references have been reported are less than 285 °C.

The results demonstrate that small amount and simple incorporation of NP-10P into PPC matrix can greatly enhance the thermal stability of the aliphatic polycarbonate, implying that the <sup>50</sup> modified PPC is more stable than pure PPC during melt processing. Moreover, this new finding can facilitate development and massive applications of this biodegradable material.

#### Thermal decomposition behaviour of PPC/NP-10P complex



**Figure. 2** The Py-GC/MS spectra of (a) PPC and (b) PPC/10wt% NP-10P complex.

Py-GC/MS is used to characterize the pyrolysates of PPC and PPC/NP-10P complex at different pyrolysis temperatures. From <sup>60</sup> the Py-GC/MS spectra (Figure 2), the presence of  $CO_2$  is confirmed by the peak at retention time 1.0–2.0 min, 1, 2-propanediol at 3.5–5.0 min, and cyclic propylene carbonate is at 7.0–10.0 min.

Figure 2(a) shows that for pure PPC at 230 °C the spectra of 65 the pyrolysates mainly appears at retention time about 3.5–5 min and 8.5-10 min, which belong to 1, 2-propanediol and cyclic propylene carbonate respectively, it clearly indicates the pyrolysis mechanism of neat PPC is chain unzipping degradation. With increasing pyrolysis temperature the unzipping product of cyclic 70 propylene carbonate is still observed and the peak intensity also increases.

As shown in Figure 2(b), for PPC/NP-10P complex, there is almost no pyrolysis product at lower pyrolysis temperature of 230 °C. With increasing pyrolysis temperature to 310 °C, with the 75 exception of cyclic propylene carbonate there is a small amount of evolved gas of  $CO_2$  occurred at retention time about 2.0 min, indicating that the thermal decomposition of PPC/NP-10P

complex at 310 °C exhibits the main chain random scission, followed by the unzipping degradation. But the peak intensity is much weaker than that of PPC at the same pyrolysis temperature, illuminating that the PPC/NP-10P complex is stable still at 310 °C. Until the purchase temperature reaches up to 280 °C.

s °C. Until the pyrolysis temperature reaches up to 380 °C, a lot of both random scission and unzipping degradation pyrolysis products produce.

The above results show that the pyrolysis mechanism of neat PPC is mainly chain unzipping degradation. But for PPC/NP-10P

<sup>10</sup> complex, main chain random scission occurs first and produces some terminal –OH groups that drastically induce the unzipping gegradation <sup>7-10</sup>; as a result, the PPC/NP-10P complex has more stable than pure PPC.

Moreover, according to the results of TGA and Py-GC/MS <sup>15</sup> measurement, we conclude that there exist the special interactions or reactions between PPC and NP-10P as indicated following discussion in detail, which leads to the improvement of thermal

stability and the change in pyrolysis mechanism of PPC.



<sup>20</sup> Figure. 3 The <sup>31</sup>P NMR spectra of NP-10P and PPC/NP-10P complex.





**Scheme 4** The end-capping reaction between PPC and NP-10P during the melt-blending process.

#### 25 Investigation of the interaction in the complex

#### <sup>31</sup>P NMR

<sup>31</sup>P NMR spectra of NP-10P and PPC/NP-10P complex are shown in Figure 3. For pure NP-10P, there are mainly two signals at 1.69 and 0.73 ppm, which are imputable to NP-10P (mono-<sup>30</sup> ester) and NP-10P (bi-ester), respectively. For PPC/NP-10P complex, the original signals that belong to pure NP-10P have disappeared and a new signal at about 0.4 ppm appears. This resonance is attributed to a <sup>31</sup>P nucleus in the NP-10P directly reacting with the PPC (Scheme 4). And the introduction of PPC, <sup>35</sup> which brings in the increase of steric hindrance and the improvement of bond angle of O-P-O, results in anti-shielding of the <sup>31</sup>P nucleus with an upfield peak shift. <sup>21, 22</sup>



Figure. 4 The FTIR spectra of PPC/NP-10P complex, PPC and  $_{40}$  NP-10P.

#### FTIR

FTIR spectroscopy is utilized to probe the interactions between the PPC matrix and NP-10P in the complex. PPC displays two strong bands at 1747 and 1235 cm<sup>-1</sup> (Figure 4), assigned to the <sup>45</sup> stretching vibrations of C=O group and C-O-C bond of the carbonate group, respectively. They do not change their positions with increasing the content of NP-10P. It indicates that there is no hydrogen bonding interaction between the PPC and NP-10P. NP-10P has a strong band at 3436 cm<sup>-1</sup> (Figure 4), assigned to the <sup>50</sup> stretching vibration of -OH group. However, there is no stretching vibration of hydroxyl group in the PPC/NP-10P complex. It is speculated that the reaction have happened between PPC and NP-10P (Scheme 4), which is in accordance to the result of <sup>31</sup>P NMR spectra.

#### 55 Intrinsic viscosity measurement

Table 2 The  $[\eta]$  of PPC and PPC/NP-10P complex.

sample	[η]
Pure PPC	103.7
PPC/1 wt % NP-10P	112.9
PPC/5 wt % NP-10P	101.3
PPC/10 wt % NP-10P	105.6

The intrinsic viscosities of the PPC and PPC/NP-10P complex are determined by using THF as a solvent. The results for PPC and PPC/NP-10P complex are listed in Table 2. The intrinsic <sup>60</sup> viscosities of both PPC and PPC/NP-10P complex are almost the same order of magnitude. This evidences that the NP-10P has no effect on the chain extension or cross linking of PPC.

### Mechanism analysis for thermal stability improving of PPC/NP-10P complex

It has confirmed that there is end-capping reaction between components in the PPC/NP-10P complex. In order to quantitatively evaluate the effect of structure and amount of NP-10P on the end-capping reaction, the theoretical calculation has been carried out. According to the results of <sup>31</sup>P NMR, it has 70 confirmed that the NP-10P is the mixture of mono- and biphosphoric ester, in which the contents of mono- and biphosphoric ester are about 62wt% and 38wt% respectively. Moreover, as according to manufacturer the PPC given is a polymer with bi-hydroxyl end group, therefore, the hydroxyl group is less than 0.76% in mole content in PPC with number average molecular weight of  $2.7 \times 10^4$ . It has calculated that when s the content of NP-10P is about 4wt%, the hydroxyl group in NP-

10P can be enough for complete end-capping of PPC.



**Figure**. 5 The thermal degradation temperature of pure PPC, NP-10P and PPC/NP-10P complex.

- As previously mentioned, the pyrolysis mechanism of neat PPC is mainly chain unzipping degradation. The  $T_{5\%}$ ,  $T_{50\%}$  and  $T_{max}$  of pure PPC are 180.6 °C, 229.3 °C and 228.8 °C, respectively (Figure 5). After adding 1wt% NP-10P, note that it is not saturated for complete end-capping of PPC, there is the end-
- <sup>15</sup> capping reaction between components and a part of end-initiated depolymerization is inhibited. So the pyrolysis mechanism of PPC/1wt% NP-10P complex is both chain unzipping degradation and chain random scission followed by chain unzipping. Thus, as shown in Figure 5, the thermal stability of PPC/NP-10P complex
- 20 is improved as compared with pure PPC, which is about 74 °C higher than that of pure PPC.

At the 5wt% NP-10P loading, the hydroxyl group in NP-10P can be enough for completely end-capping PPC. The pyrolysis mechanism of PPC/5wt% NP-10P complex is chain random

- $_{25}$  scission, followed by the chain unzipping. So the thermal stability of PPC/5wt% NP-10P complex is higher than PPC/1wt% NP-10P complex. Additionally, the  $T_{5\%}$  of PPC/5wt% NP-10P complex is 258  $^{\circ}\mathrm{C}$  as shown in Figure 5, which indicates that the chain scission depolymerization has been happened at this temperature.
- <sup>30</sup> As continuously increasing the content of NP-10P, at 10wt% or 15wt% NP-10P loading, the content of NP-10P is supersaturated for complete end-capping of PPC. On the one hand, NP-10P can completely end-cap with PPC, which leads to the pyrolysis mechanism of PPC/NP-10P complex is chain random scission,
- <sup>35</sup> followed by the chain unzipping; on the other hand, the excess NP-10P can also continue end-cap the fractured chain of PPC, and inhibit the occurrence of chain unzipping that is caused by the chain scission. So the thermal decomposition temperature of PPC/NP-10P complex, in which the content of NP-10P is
- 40 supersaturated, is gradually enhanced again.

#### Conclusions

The thermostable PPC/NP-10P complex by the use of a simple melt-blending method has been prepared in the present work. NP-10P can significantly improve the thermal stability of PPC matrix,

- <sup>45</sup> in particular, with only 1 wt% of NP-10P incorporated into the PPC, about 74 °C increase in decomposition temperature with 5% loss in weight is found. It is due to the fact that the PPC is endcapped with NP-10P, which has confirmed by the <sup>31</sup>P-NMR, FTIR, and intrinsic viscosity measurement. And it also leads to
- <sup>50</sup> the change in pyrolysis mechanism of PPC, which varies from chain unzipping degradation to chain random scission followed by the unzipping degradation. Moreover, this new finding will facilitate development and massive applications of this biodegradable material in the future.

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#### A novel method to improve the thermal stability of Poly (propylene carbonate)

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#### Highlight

The introduction of NP-10P by simple melt-blending can significantly improve the thermal stability of PPC. This new finding will facilitate development and massive applications of this biodegradable material.

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