In situ reinforced and flame-retarded polycarbonate by a novel phosphorus-containing thermotropic liquid crystalline copolyester

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ARTICLE INFO

ABSTRACT

Polycarbonate (PC) was blended with various loadings of novel phosphorus-containing thermotropic liquid crystalline copolyester named PHDDT to form the *in situ* reinforced composites (PC/PHDDT) by flake extrusion. The morphology, thermal behaviors, tensile properties and flame-retardant performances of PC/PHDDT composites were investigated. Results suggested that fine deformation and microfibrillation of PHDDT in PC matrix could be formed during flake extrusion, which was confirmed by both the SEM observation and rheological analysis. With the increase of PHDDT content, the limiting oxygen index (LOI), tensile strength and storage modulus of the composites were enhanced simultaneously, along with the gradually decreased values of the peak heat release rate (PHRR) and the total heat released (THR), indicating the *in situ* reinforced and flame-retardant PC/PHDDT composites could be obtained.

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1. Introduction

Polycarbonates (PC), especially the aromatic ones (such as bisphenol A PC), are widely known for special applications due to their outstanding mechanical properties, heat resistance, dimensional stability, transparency and exceptional clarity. For instance, PC has been used as engineering thermoplastics in various industrial fields such as electrical & electronic equipments, automobile, construction and packing, etc. Because of a large number of aromatic rings and a high tendency to charring, PC itself shows a V-2 rating in the Underwriters Laboratories 94 (UL-94) test, which means a better flame-retardant property than other thermoplastics. However, more stringent flame-retardant performance is often required in some special fields, thus it becomes very necessary to enhance the flame retardance of PC [1]. Meanwhile, it is unsatisfied that most flame-retardant additives will reduce the mechanical properties of PC simultaneously while improving its flame retardance.

Thermotropic liquid crystalline polymers (TLCPs) have good thermal stability [2,3], outstanding chemical resistance [4,5], high strength, high modulus and excellent mechanical properties [6,7], as well as low linear viscosity in liquid crystalline state [8,9], which make them become attractive high performance engineering materials for offering numerous applications [10,11]. Also, the presence of a high modulus and high strength TLCP as a dispersed phase in an engineering plastic can act as a "processing aid" to reduce the viscosity of the matrix [12], and microfibrils of the TLCP can be formed "*in situ*" to significantly alter the mechanical properties of the blended materials. Various types of commercial liquid crystalline polymers, such as Vectra™, have been reported to blend with polypropylene (PP), polycarbonate (PC), and poly(ethylene terephthalate) (PET) etc. to form the so-called *in situ* reinforced composites [13,14]. With the concept of *in situ* reinforced composites coming up, reinforcing effect was mostly determined by the morphology of TLCP in the matrix. Usually, the resulting fibrils with a high aspect ratio show in better reinforcing ability. Therefore the factors influencing the fibrillation of TLCP in matrix become hotspots [15—18]. Generally speaking, the viscosity ratio of TLCP to the matrix [8], the type and intensity of flow field [15,16], the compatibility of TLCP and the matrix [17], TLCP content and the interfacial tension [18], are considered as the basic factors for the fibrillation of TLCP in matrix. Meanwhile, adding the third component could influence the morphology of TLCP in the matrix such as glass beads, $CaCO_3$ whisker and nano-clay [19—21]. Introducing the flame-retardant elements into the molecules of TLCP before blending the TLCP into the required polymer matrix to form the *in situ* composites is considered to be a good way to resolve the contradiction between flame retardance and mechanical properties.

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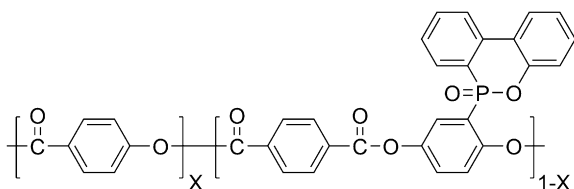
Scheme 1. Chemical structure of TLCP$_{Ar}$, where X and $1-X$ denote the overall composition in molar ratio, not the block length.

Fig. 1. The second heating DSC curves for neat PC, PHDDT and PC/PHDDT composites in different weight ratio (95/5, 90/10, 85/15 and 80/20).

A kind of wholly aromatic thermotropic liquid crystalline copolyester containing phosphorus (TLCP$_{Ar}$, Scheme 1) with high flame retardance (LOI of 70) had been synthesized to prepare *in situ* reinforced flame-retardant composites which have both good flame retardance and better mechanical properties simultaneously [22–25]. However, TLCP$_{Ar}$ with a wholly aromatic constitution is hard to melt (T_m of 290 °C) during processing, which limits its wider application. In order to solve this problem, a novel wholly aromatic liquid crystalline copolyester named as poly(-hydroxybenzate-*co*-DOPO-benzenediol dihydrodiphenyl ether terephthalate) (PHDDT, Scheme 2) has been prepared by introducing 4, 4′-dihydroxydiphenyl ether (DADOP) as a kinked unit into the main-chain of TLCP$_{Ar}$ to lower the thermal transition temperatures [26].

In this article, investigation has been carried out on the flame retardance of PC composites *in situ* reinforced by the phosphorus-containing TLCP, PHDDT with high flame retardance, lower transition temperature and relatively broader mesophase temperature range. PHDDT was added into PC matrix through twin-screw extrusion. Influence of PHDDT on comprehensive properties of the PC/PHDDT *in situ* composites including morphology, rheological and mechanical properties, thermal behaviors, thermal stability and flame retardance were discussed.

2. Experimental part

2.1. Materials

Bisphenol A Polycarbonate (PC) was purchased from Dow Chemistry Company (CALIBRE 201-15) with a melt index of 15 g/10min and a room temperature density of 1.2 g/cm^3. PHDDT used in this study was synthesized by melting transesterification from *p*-acetoxybenzoic acid (*p*-ABA), terephthalic acid (TPA), 2-(6-oxid-6H-dibenz<c,e><1,2>oxaphosphorin6-yl)1,4-benzenediol (DOPO-HQ), and 4,4′-diacetoxydiphenyl ether (DOP) at the overall molar ratio of 10:5:4:1, with an intrinsic viscosity of 1.68 dL/g as determined at 30 °C in phenol/tetrachloromethane (volume ratio, 1:1) mixed solvent. The synthesis and properties were fully described in the authors' previous work [26].

2.2. Preparation of PC/PHDDT composites

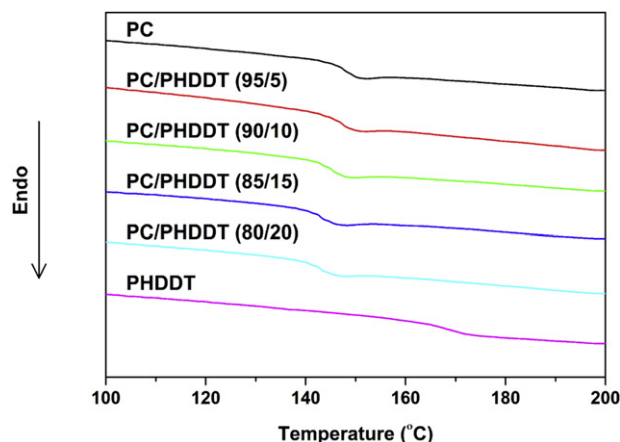PC and PHDDT were dried under vacuum at 120 °C for 12 h before extrusion. Then, PC was blended with different PHDDT loadings at 5, 10, 15 or 20 wt% using a HAAKE Rheomex 254 twin-screw extruder together with a HAAKE Postrx to squeeze out flake specimens with 1 mm thickness. Zone temperatures are 235, 245, 245, 240 °C from feeding region to die, respectively. Standard bars for cone calorimetric analysis and limit oxygen index (LOI) experiments were prepared by compression molding at 250 °C.

2.3. Thermal analyses

Thermal transition temperatures of neat PC, PHDDT and PC/PHDDT composites were measured by using a differential scanning calorimeter (DSC TA Q200 1747) at a heating rate of 10 °C/min from 40 to 300 °C in a continuous nitrogen flow. The instrument was calibrated for both heat flow and temperature using indium and zinc standards in advance. To minimize variations of sample preparation history, all DSC runs were obtained from the second heating cycle.

Dynamic mechanical analysis (DMA) of the flake specimens (16.0 × 8.0 × 0.8 mm^3) were tested via a dynamic mechanical analyzer (DMA TA Q800) at a heating rate of 5 °C/min from 40 to 200 °C under tension clamp.

Thermogravimetric analysis data of the composites with different PHDDT contents were obtained from a Netzsch TG 209 F1 (Germany) instrument at a heating rate of 10 °C/min from 40 to 700 °C under a nitrogen flow.

2.4. Morphological observation

The morphology of the composites with different PHDDT contents were observed by an FEI (INSPECT F) SEM instrument with an acceleration voltage of 10 kV. The observed specimens were prepared by cryogenically fracturing in liquid nitrogen. A thin layer of gold was then sprayed on the fractured surface prior to SEM observations.
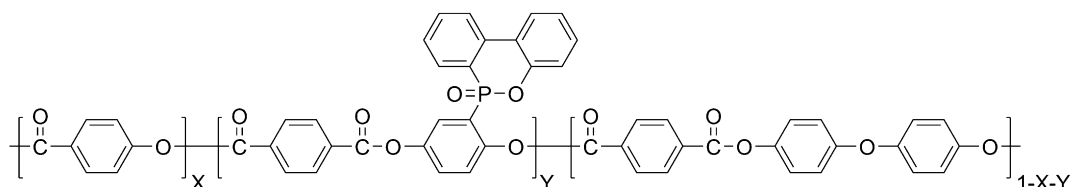
Scheme 2. Chemical structure of PHDDT, where X, Y, and $1-X-Y$ denote the overall composition in molar ratio, not the block length.

Table 1
Results obtained from DSC (heating rate = 10 °C/min), DMA (heating rate = 5 °C/min) and TGA (heating rate = 10 °C/min).

PC/PHDDT	T_g^{DSC}(°C)[a]	DMA parameters			TGA parameters		
		T_g^{DMA}(°C)[a]	Storage modulus (MPa)	Loss modulus (MPa)	$T_{5\ wt\%}$ (°C)	T_{max} (°C)	Residues at 700 °C (wt%)
100/0	147.6	164.1	2006	353	470.4	521.7	22.8
95/5	147.3	162.4	2494	397	429.9	474.6	20.1
90/10	145.4	160.1	3315	441	421.7	459.2	22.3
85/15	142.9	160.8	3800	445	417.9	450.6	23.0
80/20	143.0	162.9	4200	499	413.8	447.1	24.7
0/100	167.5	–	–	–	433.1	489.4	44.1

[a] T_g^{DSC} and T_g^{DMA} represent the glass transition temperatures of all samples tested via DSC and DMA, respectively.

2.5. Rheological characterization

Dynamic oscillatory rheological measurements of neat PC and PC/PHDDT blends were performed with a parallel-plate fixture (8 mm diameter and 1 mm thickness) using an Advanced Rheometric Expansion System (ARES, Bohlin Gemini 200) in the oscillatory shear mode. The complex viscosities ($|\eta^*|$) were measured as a function of frequency ranging from 0.01 to 100 Hz at three different temperatures of 240, 250, and 260 °C, which were much closer to the processing and injection molding temperatures. Results were found to be well within the linear viscoelasticity range of the investigated materials.

2.6. Tensile properties

The samples for tensile property measurements were prepared by directly cutting from the extruded sheet. Tensile properties of the samples were measured at the parallel orientation of the fibers by a universal material testing machine (CMT6503, Shenzhen SANS Test Machine Co., Ltd.) at room temperature according to ISO 527-5: 1997 (Plastics - Determination of tensile properties - Part 5: Test conditions for unidirectional fiber-reinforced plastic composites). Values of tensile properties reported here were the averages of at least five individual measurements.

2.7. Flame retardance and combustion behaviors

LOI tests were carried out with an HC-2 oxygen index test instrument (Jiangning County, China) according to the standard limiting oxygen index test, ASTM D 2863-97. Testing bars of the samples with the dimensions size of 130.0 × 6.5 × 3.2 mm³ were compression-molded in 10 MPa at 240 °C. The cone calorimeter tests were determined by a Fire Testing Technology Limited (FTT) cone calorimeter (East Grinstead, UK), according to the procedures of ISO 5660-1. Compression-molded square specimens with the dimensions size of 100.0 × 100.0 × 6.0 mm³ were irradiated at an external heat flux of 50 kW/m². Typical results from cone calorimeter tests were reproducible within ±10%.

3. Results and discussion

3.1. Thermal behavior

The DSC thermograms of neat PC, PHDDT and their composites are shown in Fig. 1. Considering the same thermal history of the prepared samples, the results of the second heating scans are discussed. The glass transition temperatures (T_g) are summarized in Table 1. Firstly, it can be observed that PC is a typical glassy polymer with the glass transition at 147.6 °C; while PHDDT is a kind of random liquid crystalline copolyester with a single T_g at 167.5 °C. It is generally believed that if the two components have poor compatibility, their composites should have two separated T_g; hence, if the composites show a single T_g, it means the two components are compatible [27]. In Fig. 1, all composites show one single T_g that decreased firstly, then increased with the increasing PHDDT content which indicates that PC and PHDDT should have good compatibility during extrusion. Furthermore, increased T_g with the increasing PHDDT content may also relate to the continuous PHDDT phase morphology observed from SEM images as follows. This variation trend of the T_g as a function of PHDDT content, as shown in DSC heating scans, may be attributed to the reactions between PHDDT and PC during the melt processing [28]. Meanwhile, the decarboxylation resulting from acidolysis of PC by the end group of
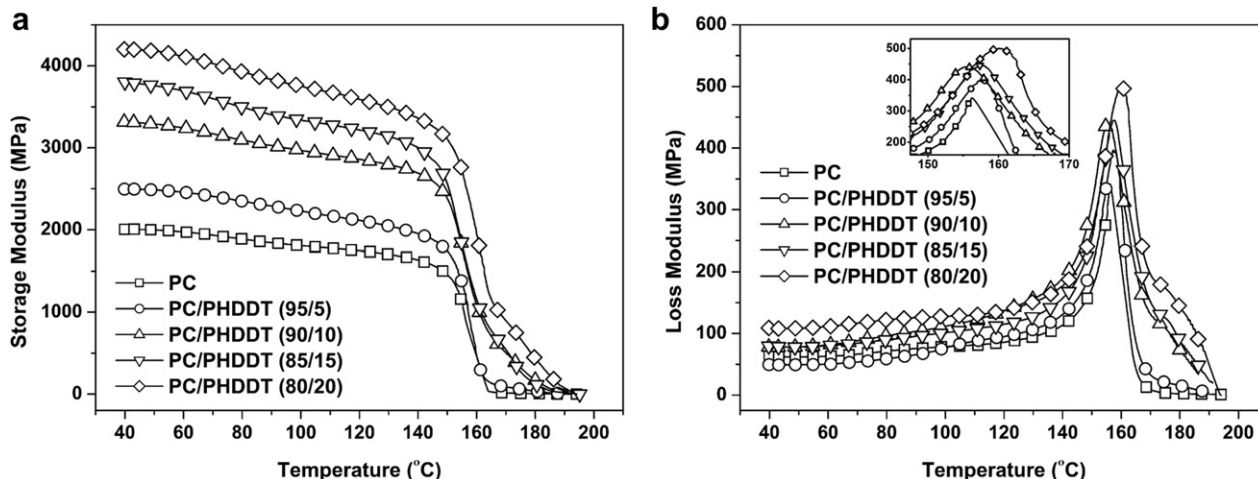

Fig. 2. The storage modulus (a) and loss modulus (b) curves for neat PC and PC/PHDDT composites in different weight ratio (95/5, 90/10, 85/15 and 80/20).
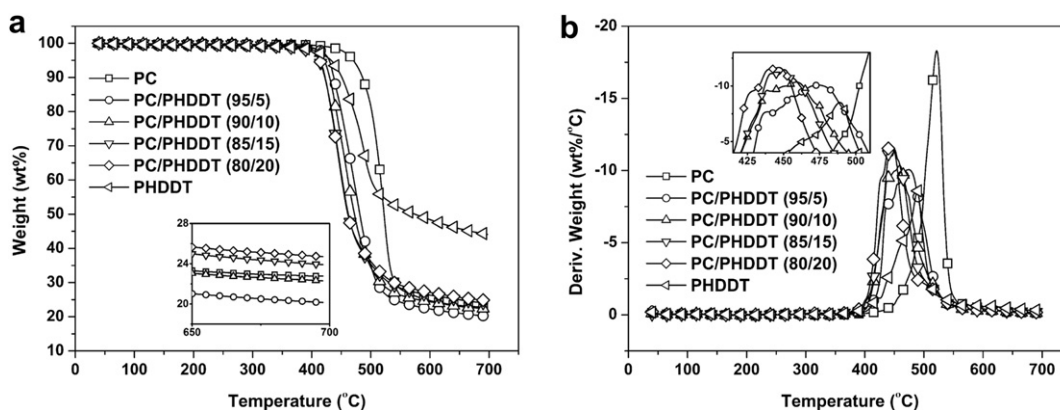
Fig. 3. Thermogravimetric (a) and derivative thermogravimetric curves (b) for neat PC, PHDDT and PC/PHDDT in different weight ratio (95/5, 90/10, 85/15 and 80/20).

PHDDT may cause partial thermal degradation to the PC matrix, which resulted in the slight decrease of T_g. While more PHDDT were involved, the rigidity of the chain should decrease the flexibility of the composites, hence the T_g got increased. However, the T_g of the composites is much closer to that of neat PC, so more evidences are necessary to further prove the compatibility [29]. Fig. 2 (a) and (b) show the curves of storage modulus and loss modulus for neat PC and the composites, respectively. With the increase of PHDDT content, both the storage modulus and loss modulus of composites increase, which means PHDDT plays a role to increase the chain rigidity.

Fig. 3 shows the TGA and DTA traces of neat PC, PHDDT and their composites in nitrogen, typical parameters are summarized in Table 1. It is noticeable that all the composites show one single degradation process. The temperatures of 5 wt% loss ($T_{5\ wt\%}$) and maximum loss (T_{max}) of the neat PC and PHDDT are 470.4 °C, and 521.7 °C, 433.1 °C and 489.4 °C, respectively. Compared to neat PHDDT, PC/PHDDT composites have lower $T_{5\ wt\%}$ and T_{max}, which would further decrease with increase of PHDDT content. In this case, when the PC matrix began thermal degradation, PHDDT had already formed a lot of dense charring layer, which could stop the inflammable gas escaping from the inside of the char and provide a positive influence on the flame retardance of PC. It is clear that the ester–ester interchange reaction could occur between two poly-condensates under heating [28,30], the reason for the early occurred $T_{5\ wt\%}$ and T_{max} of the composites should be attributed to the above-mentioned reaction between PC and PHDDT. At the region above 550 °C, curves of neat PC and PC/PHDDT composites

were similar to each other, but the thermal stability of the composites are better than that of neat PC as the PHDDT content reaches 15 wt%, same as the residual char yield and the maximum degradation rate, which should provide a positive influence on the flame retardance of PC. It is noticeable that the composites containing 5 or 10 wt% PHDDT show a lower char yield than the neat PC, which could be explained that the end carboxyl of PHDDT speeds up the breaking of carbonate-linking groups and hence accelerates the degradation process. However the composites have a higher char yield with higher PHDDT content, it should be ascribed to the phosphorus-containing monomer of PHDDT which promotes the residual char formation during the thermal degradation process [31]. The two effects are competitive with each other, therefore, when adding less PHDDT the accelerated degradation will be the dominant phenomenon; while increasing PHDDT content the char formation becomes dominative.

3.2. Morphological observation

In this study, the fractured surfaces of the PC/PHDDT composites have been observed by SEM. The images at the direction perpendicular (a) and parallel (b) to the fiber orientation are shown in Fig. 4. Fig. 4 (a-1) and (b-1) exhibit the fractographs of the flake specimens PC/PHDDT (95/5) at the direction perpendicular (a) and parallel (b) to the fiber orientation. It is clear that PHDDT phase is dispersed well as straight fibrils in PC matrix with an elongated aspect ratio of 50–100. The same phenomenon can also be observed in PC/PHDDT (90/10), PC/PHDDT (85/15) and PC/PHDDT
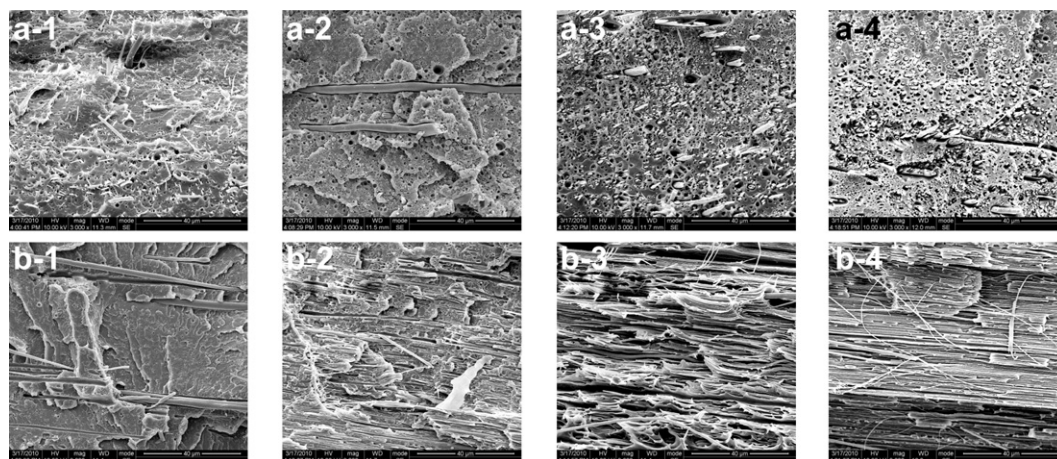

Fig. 4. Scanning electron micrographs of the cryogenically fractured surfaces at a direction perpendicular (a) and parallel (b) to the fiber orientation of PC/PHDDT composites in different weight ratio: 1, 95/5; 2, 90/10; 3, 85/15; 4, 80/20.
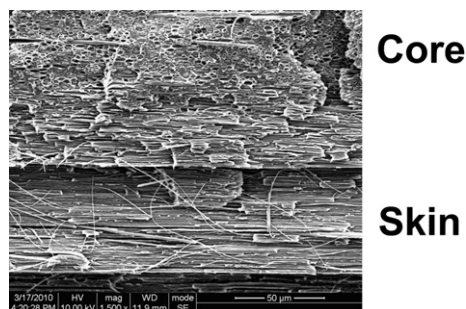
Fig. 5. Typical skin-core heterogeneous dispersion of the PHDDT microfibrils in PC matrix: scanning electron micrograph of PC/PHDDT (80/20) composite at a direction parallel to the fiber orientation.

(80/20) samples at the direction perpendicular to the fiber orientation. The increment of PHDDT content does not influence the morphology of the dispersed phase. However, with the increase of PHDDT content, the morphology of the PC matrix has been changed. Adding 5 wt% PHDDT the morphology of PC matrix is smooth; however, it is observed that PC phase turns to stratiform structure with more PHDDT.

Generally, blending of a rigid-rod TLCP with flexible-coil polymers is not favorable in thermodynamics [14], which means the TLCP microfibrils are unstable and tend to relax or break up at the temperature above the melt point of TLCP. Under an appropriate processing condition, TLCP phase tends to deform into microfibrils in the skin layer, while it is dispersed as ellipsoids or spherical domains in the core region of the *in situ* composite. However, in a compatibilized composite, much finer, longer and uniformly distributed TLCP fibrils could be formed in the matrix. In this case, a typical skin-core heterogeneous distribution of PHDDT microfibrils
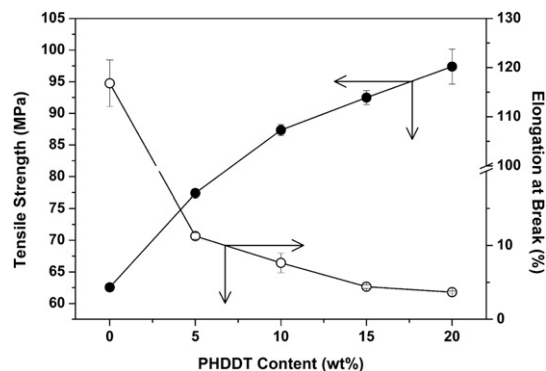

Fig. 7. Values of tensile strength and elongation at break of the PC/PHDDT composites as a function of PHDDT content.

in PC matrix of PC/PHDDT (80/20) composite is shown in Fig. 5, indicating a poor compatibility between PHDDT and PC phases and the different shearing velocity and cooling rate from skin and core region during processing. The diameters of the fibrils become larger from skin to core section (from bottom to top of Fig. 5). Furthermore, looking from the direction perpendicular to the fiber orientation, there are some micropore between PHDDT phase and PC phase, indicating that the two phases are not totally compatible as the DSC results suggested, which would play a positive role on the microfibrillation of PHDDT [32].

3.3. Rheological characterization

Fig. 6 shows the complex melt viscosities of the composites with different oscillation frequencies at 240, 250 and 260 °C. It is
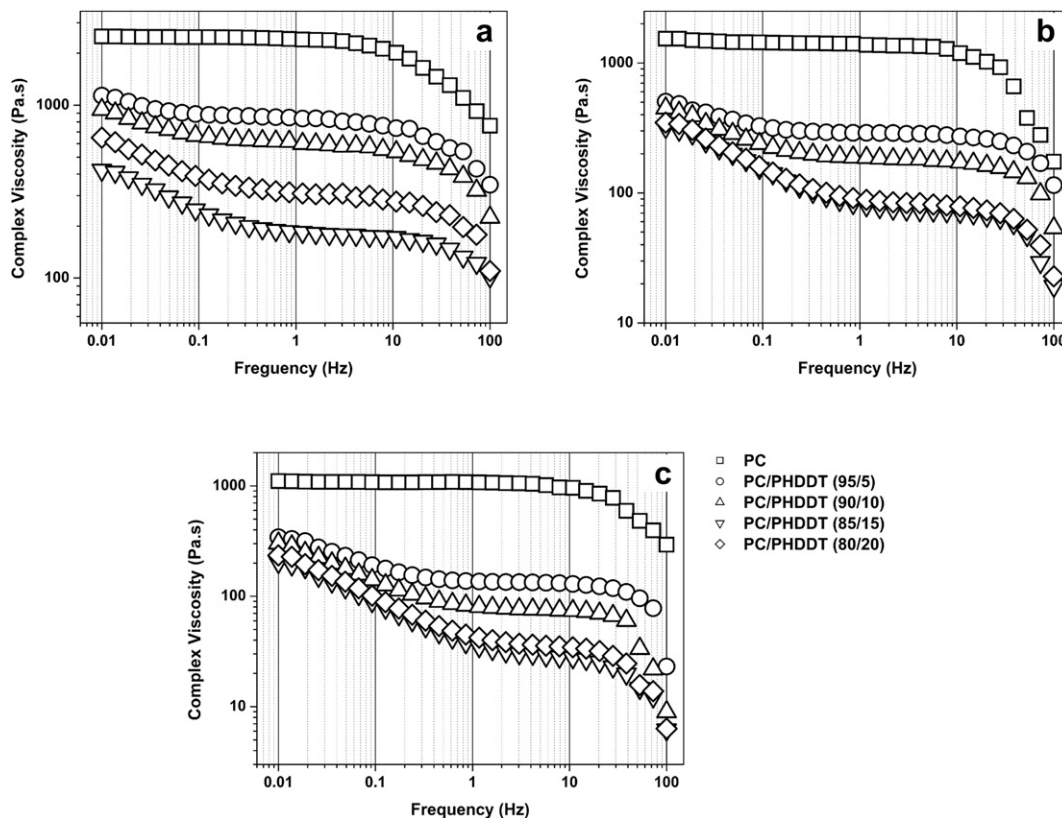

Fig. 6. Complex melt viscosity plotted against oscillation frequency at 240 (a), 250 (b) and 260 °C (c) for PC and PC/PHDDT composites in different weight ratio (95/5, 90/10, 85/15 and 80/20).
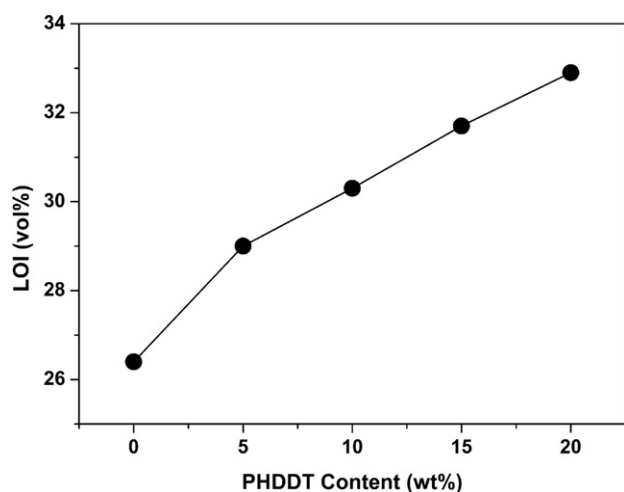
Fig. 8. LOI values of PC/PHDDT composites with different PHDDT content.

noticeable that the testing temperatures as well as PHDDT content considerably affected the complex viscosities of the composites. It is observed that the viscosity curves at different temperatures are similar, shear viscosities of all composites decreased with increase in shear rate (oscillation frequency), and decreased almost monotonously with increase in PHDDT content, which exhibits a typical shear thinning behavior to improve melt processability of the composites. Therefore, PHDDT can function as a processing aid by reducing the melt viscosity of the blend system during compounding, thereby easing the processability of the thermoplastic composites [12]. Interestingly, the shear viscosity of the composite with 20 wt% PHDDT is a little higher than that with 15 wt% PHDDT, and the viscosity difference between the composites with 20 and 15 wt% PHDDT decreases with increase of the testing temperature. It is well-established nowadays that the complex viscosity of a binary or ternary polymer blend is very sensitive to its morphological state [30]. Combining the viscosity analyses and morphological observation, it is easy to conclude that better deformation and microfibrillation of PHDDT in the composites accord well with the lower complex viscosity of the composites. That is to say, the finer PHDDT microfibrillation contributes to the larger viscosity decrease from the PC/PHDDT composites [33,34]. Also, it should be noticed that the curves of neat PC and the composites are totally different. Taking Fig. 6 (a) as an example, neat PC shows Newtonian flow behavior at low frequencies. At the frequency region lower than 10 Hz, the

viscosity of neat PC does not have significant change; with higher oscillation frequency, it is reduced dramatically, exhibiting a typical pseudoplastic fluid behavior. However the decrement of viscosities of composites could be divided into three regions. With increasing oscillation frequency the decline range of different region is not identical. At the regions with frequency lower than 0.04 Hz and higher than 28.07 Hz, the extent of the reduction is higher than that at the medium frequency region. Generally, transesterification between PC and PHDDT could average the molecular size of both polymers [35]. Not only the molecular weight of PC will be dramatically reduced, but also the molecular weight distribution will become much wider. In this case, with the increase of PHDDT content, the frequency range of the Newtonian plateau for the composites becomes gradually narrow down, indicating the increase of the molecular weight distribution [36], which may be caused by the reactions between PC and PHDDT during tests.

3.4. Tensile properties

Fig. 7 shows the values of both tensile strength and elongation at break of neat PC and the PC/PHDDT composites. The tensile strength of PC/PHDDT composite was increased monotonously with increase of PHDDT content, and reached 97.4 MPa from 62.6 MPa of neat PC with 20% PHDDT addition. However, the elongation at break became much smaller in all composites, which failed in a more brittle behavior beyond yielding during test. There are two reasons for the sharp decrease of the elongation at break. On one hand, apparently the microfibrillation of PHDDT with strong rigidity in all composites greatly affects the elongation at break of the PC/PHDDT composites due to the lower ductility in the composites, which results from the higher reduction of the molecular mobility of the matrix [37]; on the other hand, the compatibility of two phases is not so good. In addition, the micropores in the interfacial region lower the superficial adhesion between the microfibrils and the PC matrix.

3.5. Flame retardance and combustion behaviors

LOI test is one of the most useful tools to evaluate whether the materials are flame-retarded in air. Generally, if the LOI value of an established plastic is less than 22, it should be associated to an inflammable material, and higher than 27 means flame-retardant; while the plastic with an LOI value between 22 and 27 belongs to flammable material [38]. Fig. 8 shows the LOI values of different
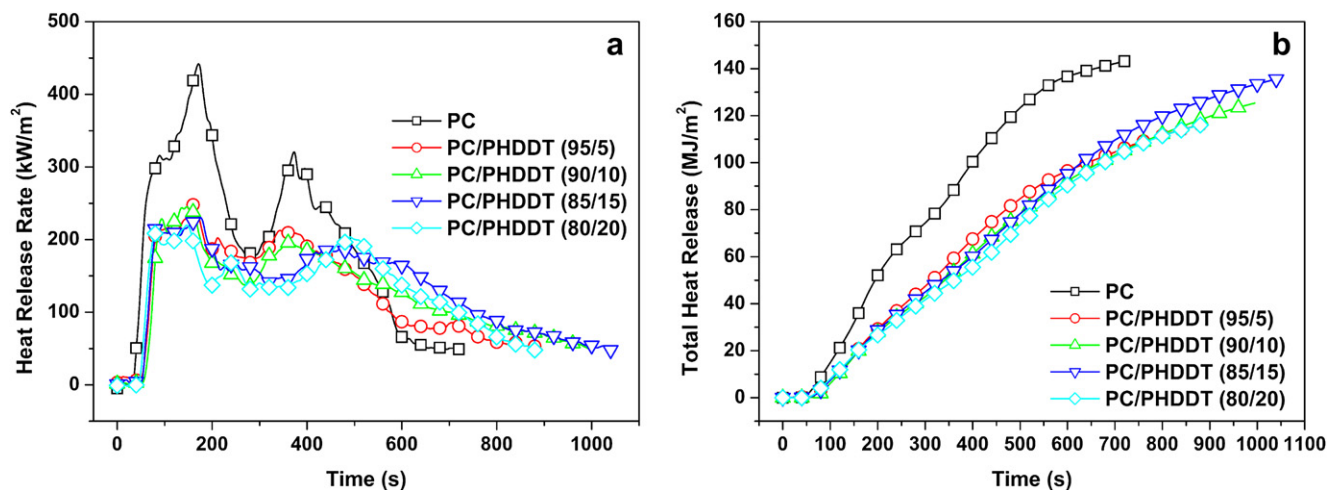

Fig. 9. Heat release rate (a) and total heat release (b) curves of neat PC and PC/PHDDT composites in different weight ratio (95/5, 90/10, 85/15 and 80/20).

Table 2
Cone calorimetric results of neat PC and PC/PHDDT composites.

PC/PHDDT	TTI (s)	PHRR$_1$ (kW/m^2)	PHRR$_2$ (kW/m^2)	TTPHRR$_1$ (s)	TTPHRR$_2$ (s)	THR (MW/m^2)	Residues (wt%)
100/0	57	453.53	323.45	170	375	142.20	19.76
95/5	48	247.81	212.91	160	340	104.53	24.62
90/10	52	246.20	195.87	135	360	103.21	20.15
85/15	50	231.03	186.72	175	445	109.62	23.16
80/20	43	220.55	205.05	145	490	102.67	22.56

PC/ PHDDT composites. The LOI value of neat PC is about 26 due to the relatively high tendency to charring, so it has certain fire resistance; however, it cannot meet the demand of some applications. It is clearly showed that the addition of PHDDT enhances the LOI value and with only 5 wt% PHDDT the LOI value has been raised to 29, which achieves the flame-retardant standard. Further, the flame retardance of the composite linearly increases with increase of PHDDT content, and the sample with the highest PHDDT content reaches LOI value of 33.0.

The cone calorimeter is widely used by fire safety engineers and researchers interested in quantitative material flammability analysis. It remains one of the most useful bench-scale tests that attempts to simulate real-world fire conditions [39]. Parameters including time to ignition (TTI), peak heat release rate (PHRR), time to achieve the peak heat release rate (TTPHRR) and total heat released (THR) are employed to evaluate the flammability of the specimens. In this case, all materials show heat release rate (HRR) curves (Fig. 9(a)) which are typical for char-forming materials [40]. Each curve shows two peaks of HRR (PHRR$_1$ and PHRR$_2$), the first one appearing at around 150 s is typical for char-forming, the other coming at around 400 s is due to the defective char bursts under high temperature for a long time, therefore a lot of inflammable gas escapes from the inside of the char. The PC/PHDDT composite has a much lower PHRR value (both PHRR$_1$ and PHRR$_2$) than that of neat PC. When adding 5% PHDDT, PHRR$_1$ and PHRR$_2$ values decreased by 195.62 and 110.54 kW/m^2 (approximately 44 and 34% of the HRRs of neat PC), respectively. With higher PHDDT content, PHRR$_1$ has no obvious decreasement. Comparing PC/PHDDT composites with neat PC, PHRR$_2$ of PC/PHDDT(85/15) and PC/PHDDT(80/20) appeared later, and the value is much lower due to PHDDT component which promotes dense char layer forming of neat PC during combustion process. It is noticeable that TTI of the composites are shorter than neat PC that is because of PHDDT cause the PC matrix partial thermal degradation. Fig. 9(b) shows the curves of total heat release (THR) of PC and PC/PHDDT composites. It is obviously that both the maximum value and gradient of the THR curves of all composites are much lower than those of neat PC; however, with increase of PHDDT content, curves of all the composites do not have a significant change (Table 2), which is in accord with the mass loss behavior during cone calorimetric (not showed here) and TG analysis.

4. Conclusion

PC/PHDDT *in situ* composites were prepared by flake extrusion. The PHDDT phase dispersed as microfibrils in the specimens and the amount of microfibrils increased with increase of PHDDT content. Decrease of the complex viscosity of the composites also confirmed the fine deformation and microfibrillation of the dispersed PHDDT phase in PC matrix. However, typical skin-core heterogeneous dispersion could be observed from the scanning electronic microscope since the compatibility between PHDDT and PC matrix is not good enough and the different shearing velocity and cooling rate from skin and core during the processing. Accordingly, the tensile strength of composites was enhanced

monotonously with increase of PHDDT content, and the increase reached 50% with highest PHDDT content (20 wt%). Nevertheless, addition of PHDDT shows a great negative influence on elongation at break of the composites, which could be attributed to the rigidity of PHDDT and poor interfacial adhesion between the dispersed microfibrillar PHDDT phase and the PC matrix phase.

The glass transition temperature (Tg) determined by both DSC and DMA decreased firstly then raised again with increase of PHDDT content, indicating a certain degree of transesterification between PHDDT and PC occurred during processing. Introduction of PHDDT decreased the initial thermal decomposition temperature ($T_{5\ wt\%}$) obviously, which could also be attributed to the interchange reaction between the two component during thermal degradation. During thermogravimetric analysis, char residues of the composites increased with increase of PHDDT content, while the temperature is higher than 550 °C, the thermal stability of the composite containing PHDDT are better than that of neat PC as the PHDDT content reaches 15 wt%, which would provide a positive influence on the flame retardance of PC.

PHDDT was beneficial to improve the flame retardance of the PC/PHDDT composite, the PC/PHDDT composite had a much lower PHRR value (both PHRR$_1$ and PHRR$_2$) than that of neat PC when adding 5 wt% PHDDT, PHRR$_1$ and PHRR$_2$ values decreased approximately 44 and 34%, respectively. However, with higher PHDDT content, PHRR$_1$ and PHRR$_2$ have no further obvious decrement. Comparing PC/PHDDT composites with neat PC, PHRR$_2$ of PC/PHDDT (85/15) and PC/PHDDT (80/20) appeared later, and the value is much lower due to PHDDT component which promote forming of the dense char layer acted as the isolated barriers. Also, both the maximum value and gradient of the THR curves of all composites are much lower than those of neat PC. Furthermore, it is observed that the LOI values of composites increased monotonously with increase of PHDDT content.

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