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Preparation and Properties of Main Chain Phosphorus Containing Poly(trimethylene terephthalate) Block Copolymers

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A series of phosphorus-containing poly(trimethylene terephthalate) multiblock copolymers were synthesized and characterized on their chemical structure, average molecular weight, thermal stability and flame retardancy. The dihydroxypropyl pentaerythritol phosphate was prepared by using 1,3-propanediol and dichloro phosphorspirol. The phosphorus-containing copolymers were prepared by transesterification and melt-polycondensation method. The results suggest that the block copolyesters were successfully prepared and it shows the characteristics of the intumescent flame retardancy. With increasing phosphorus content in main-chains, the block copolyesters show reduced initial degradation temperatures but increased char residue and gradually increased limiting oxygen index. The dichloro phosphorspirol component contributes flame retardancy in the copolyesters.

Keywords: Poly(trimethylene terephthalate), Dichloro phosphorspirol, Thermal stability, Intumescent flame retardancy.

INTRODUCTION

Flame retardancy is usually one of the absolutely necessary properties of the polymer materials for the applications in the industry or in human life. At present, most of the reactive flame retardants in polyesters are halides, which belong to non-intumescent flame retardants with serious toxicity and carcinogens in burning, especially for the brominated flame retardants that have been forbidden to be used in many countries. New flame retardants containing phosphorus compounds are rapidly developed by researchers because polymer materials containing phosphorus flame retardant do not produce toxic gas or lots of smoke, especially its intumescent effect[1]. The flame retardant containing phosphorus is a weak flame inhibitor and it plays the flame retardant effect mainly in the polymer condensed phase; however, when it is gasified, it also can slow down the combustion process. Moreover, its combustion and pyrolysis products give out less corrosive gas and toxicant. Therefore, organic phosphorus flame retardants are preferred to be used in polymer materials.

However, most flame retardants containing phosphorus are usually physically blended with polymers to prepare a material and the compatibility between phosphorus compounds and molten polyesters is often poor and that will further depresses other physical properties of the material[2,3]. If the flame retardant is imbibed by the polymer chains to made a polymer with inherent flame retardancy, the material's flame retardancy will be improved greatly without concerning the compatibility issue[4,5] and the inherent flame retardancy polymers may have more advantages in the application. The studies have confirmed that by synthesize polymers containing the flame retardants; it can effectively improve the permanent flame retardant properties of the polymers[6-9]. In recent years, a new kind of flame retardant containing phosphorus has been used in polymer materials[10]. The charred carbon chains containing phosphorus can prevent the heat transfer and reduce the diffusion of the combustible gas and thus achieve a good flame retardant effect.

The dichloro phosphorspirol (PDD) is an intermediate in the synthesis of pentaerythritol double phosphates melamine salt, which is a type of the most famous intumescent flame retardant. The molecular formula of dichloro phosphorspirol is shown in **Scheme-I**. First, due to the presence of pentaerythritol, if the polymer is heated for combustion, a dense carbon layer will be formed, which can prevent the further combustion of the copolyester. Second, three elements, phosphorus, oxygen and carbon, compose of a stable hexatomic heterocyclic ring structure in the polymer molecule, so that dichloro phosphorspirol has good thermal stability, pretty flame retardancy effect and it is environmentally friendly. Dichloro phosphorspirol is difunctional reactive flame retardant with two -Cl active groups, which can react with the compounds containing -OH, $-NH_2$, -NH- groups to form a series of intumescent flame retardants or flame-retardant polymers. Ding *et al.*[10] prepared a new flame retardant with dichloro phosphorspirol and triethanolamine and used it to modified polyester fabric. The results suggest that the modified fabric has a higher thermal stability and the amount of the carbon residue after combustion increased significantly. Ma *et al.*[11] prepared a series polyesters containing different proportions of dichloro phosphorspirol and diethyl diglycol phthalate. The results suggest that the copolyester with 3 % dichloro phos-phorspirol can self-extinguishing away from the fire. Yao *et al.*[12] prepared a flame-retarding nylon 6 by compounded *N*-methylol-3-(dimethoxy) phosphonopropioamide into macromolecular chain and the modified nylon 6 shows higher limiting oxygen index. Banerjee *et al.*[13] prepared a polyimido-phosphonate containing phosphonate and the polymer shows improved limiting oxygen index. Huang *et al.*[14] prepared nylon 66 with dichloro phosphorspirol, hexamethylenediamine and adipic acid by polycondensation method and the results suggest that the product has flame retardancy and self-extighuishing characteristics. Wang *et al.*[15] prepared chlorinated spirophosphate-bisphenol A copolymers by dichloro phosphorspirol and bisphenol A and the copolymer has a good flame retardancy for polypropylene.

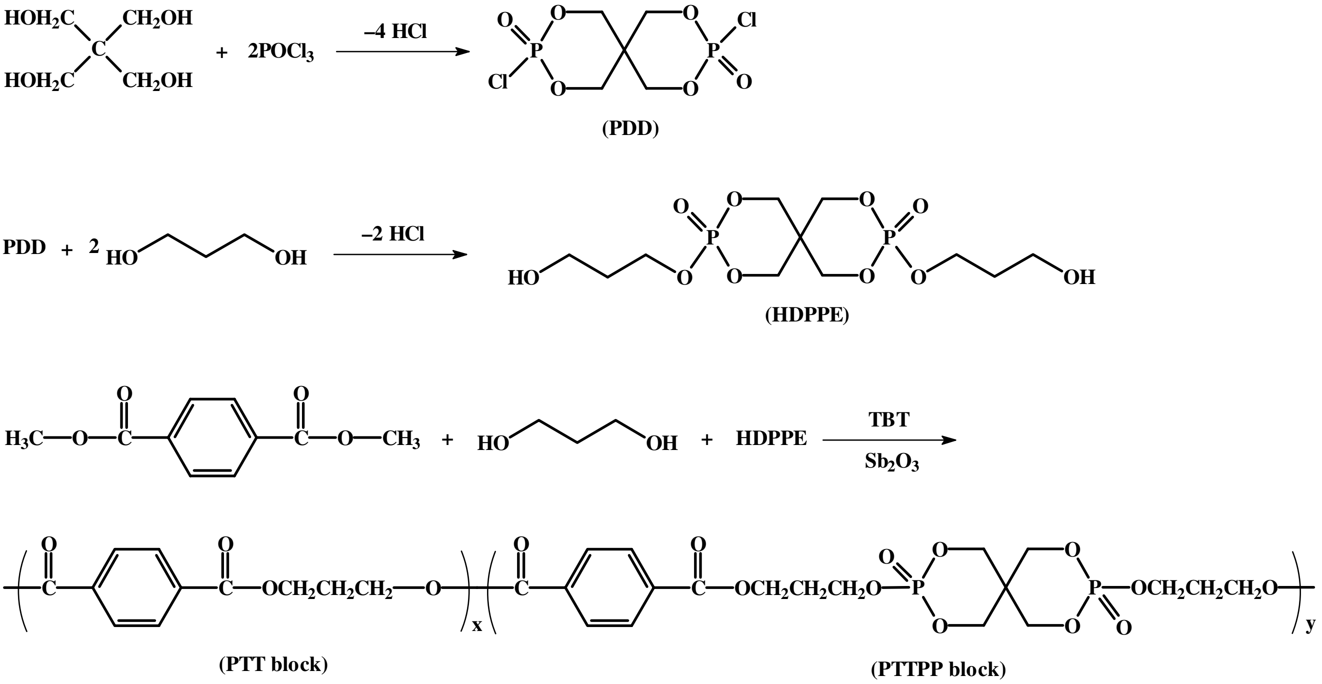
As a linear aromatic polyester, poly(trimethylene terephthalate) (PTT) was first produced by Shell Chemicals Co. under the trade name Corterra®. Compared to the other more familiar polyesters, such as poly(butylene terephthalate) (PBT), poly(ethylene terephthalate) (PET) and poly(ethylene 2,6-naphthalate) (PEN), poly(trimethylene terephthalate) has a strong competitive power due to its excellent properties[16-19]. In order to improve the flame retardancy of the poly(trimethylene terephthalate), the dichloro phosphorspirol is introduced into the molecular chain of poly(trimethylene terephthalate) to prepare a block copolyester containing dichloro phosphorspirol by melt polycondensation and its chemical structure, molecular weight, thermal properties and flame retardancy were characterized.

EXPERIMENTAL

Phosphorus oxychloride ($POCl_3$), AR, Chengdu Kelong Chemical Reagent Factory (China); Pentaerythritol, AR, m.p. = 250 °C, Beijing Hongxing Chemical Plant (China); Dimethyl terephthalate (DMT), AR, white flakes, m.p. = 139-142 °C, acid value = 0.2 (KOH mg/g), Sinopharm Chemical Reagent Co.(China); 1,3-propanediol (PDO), AR, Tianjin Guangfu Institute of Fine Chemicals (China); tetrabutyl titanate (TBT), AR, Tianjin Kermel Chemical Reagent Co. (China); antimony trioxide (Sb_2O_3), AR, Tianjin Chemical Reagent Plant III (China); tetrachloroethane, AR, Tianjin Guangfu Institute of Fine Chemicals (China).

Preparation of dichloro phosphorspirol (PDD): The synthetic reaction of dichloro phosphorspirol is shown in **Scheme-I**. 30 g Pentaerythritol and 100 mL $POCl_3$ were put into a three-necked flask, stirred and heated to 80 °C, refluxed for 1 h; then gradually heated up to 110 °C, refluxed for 12 h. After completion of the reaction, the solution were cooled to room temperature, filtrated, washed by chloroform, diethyl ether and absolute ethanol and dried for 24 h at 50 °C in vacuum oven to obtain a white solid powder. The yield of product was 67 %.

Preparation of dihydroxypropyl pentaerythritol phosphate (HDPPE): The synthesis reaction of dihydroxypropyl pentaerythritol phosphate is shown in **Scheme-I**. 50 mL chloroform and 25 mL 1,3-propanediol was added into 250 mL three-necked flask, stirred and heated to reflux, then dichloro phosphorspirol was added in increment and the reaction was not stopped until no hydrogen chloride gas was released; the molar ratio of dichloro phosphorspirol to 1,3-propanediol is 1 to 2. Finally, the solution separated into two layers, the upper layer of chloroform and the lower layer of dihydroxypropyl pentaerythritol phosphate.



Scheme-I: Synthesis of the copolymer of PTT-PTTPP

Preparation of copolymers (PTT-PTTPP): The synthesis of the copolymer of PTT-PTTPP is shown in **Scheme-I**. Dimethyl terephthalate, 1,3-propanediol and HDPPE (addition of phosphorus mass ratio as 3, 4.1, 5.4 and 6.8 %) were added into the vacuum reaction tank in certain proportion and then TBT catalyst was added (TBT:DMT = 2 × 10^{-4} mol/1 mol). Subsequently, the mixture was stirred and heated to 140 °C under N_2 protection. As the methanol distilled, the temperature was gradually risen to 220 °C. When there was nearly no methanol distilled, a few of Sb_2O_3 was added into the mixture and the temperature was risen to 230 °C under low pressures (about 10^4 Pa). When there was nearly no 1,3-propanediol distilled, the temperature was risen to 265 °C and the pressure continually decreased to about 100 Pa for further removing 1,3-propanediol and other small molecules from the system. When there was nearly no distillates, the reaction was stopped and the product was named as PTT-PTTPP copolymer.

Limiting oxygen index of the product was measured by using the oxygen index meter (HC-1, Nanjing Jiangning Analysis Instrument Co.). FTIR spectra were recorded with a Varian-640 spectrophotometer (KBr pellet technique) in the wavenumbers from 4000 to 500 cm^{-1}. The solution ^1H NMR spectra were recorded by an AVIII type 600 MHz NMR spectrometer (Bruker BioSpin Co., Germany) using deuterated dimethylsulfoxide as a solvent for dichloro phosphorspirol and F_3C_2OOD as a solvent for the copolymer and TMS as interior label. The thermal stability of the product was investigated by using thermogravimetric analysis (TGA) (Pyris 6, Perkin-Elmer Co., USA), in which the dried sample was heated from 30 to 700 °C at 20 °C/min under nitrogen. The surface morphology of the sample after burning was characterized by scanning electron microscopy (SEM) (TM3000, Hitachi, Japan). The intrinsic viscosity [η] was measured using a viscosity measuring instrument (Dc9v/0, Schott, Germany) with a Ubbelohde viscometer using mixed solvents of phenol and tetrachloroethane (1:1) at 25 ± 0.1 °C and the [η] and the average molecular weight were calculated by the following functions,

$$[\eta] = 2.11 \times 10^{-5} M_w^{0.98} \quad (1)$$

RESULTS AND DISCUSSION

Chemical structure analysis: The FTIR spectra of dichloro phosphorspirol, hydroxypropyl pentaerythritol phosphate and the copolyester (PTT-PTTPP) are presented in Fig. 1. As shown in Fig.1a, for dichloro phosphorspirol, several strong characteristic peaks were appeared at 2980 cm^{-1} (C-H stretching vibration absorption peak in $-CH_2-$), 1306 cm^{-1} (P=O double bond stretching vibration absorption peak), 855 cm^{-1} (P-O absorption peak in $P(OCH_2)C$), 1024 cm^{-1} (P-OC bond stretching vibration absorption peak), 547 cm^{-1} (P-Cl bond stretching vibration absorption peak). As seen from Fig. 1b, the peak at 545 cm^{-1} is not observed, while -OH stretching vibration absorption peak appears at 3400 cm^{-1}, indicating that P-Cl bond is substituted by the hydroxypropyl. For the copolymer, a broad peak of 3400 cm^{-1} (Fig. 1c) is corresponding to the stretching vibration of the hydroxyl group; the two bands of 2960 and 2926 cm^{-1} are corresponding to the asymmetric and symmetric stretchingvibration of the C-H bond in $-CH_2$; a peak of 1280 cm^{-1} is the stretching vibration of P=O; the P-O-C bond stretching vibration is around 1020 cm^{-1}; 850 cm^{-1} is the vibration peak of P-O bond in $P(OCH_2)C$; an ester carbonyl (-C=O) peak appears around 1730 cm^{-1}. As the polycondensation reaction proceeds, the absorption peak of -OH around 3400 cm^{-1} is decreased gradually, indicating that the transesterification reaction occurs through the ester group of the dimethyl terephthalate and the hydroxyl group of dihydroxypropyl pentaerythritol phosphite.

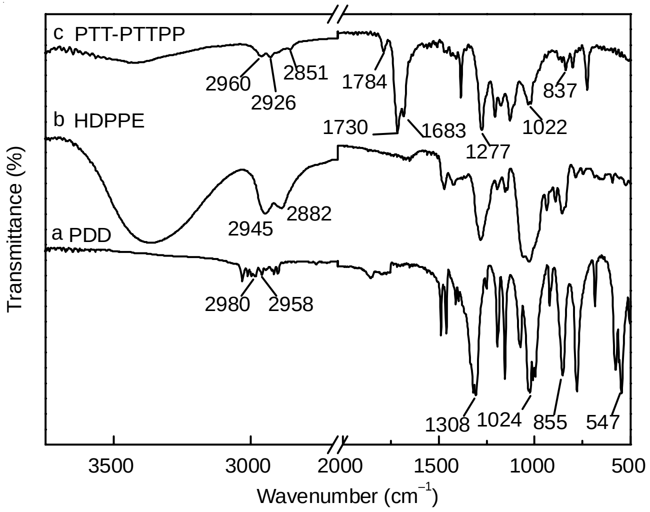


Fig. 1. FTIR spectra of dichloro phosphorspirol, HDPPE and PTT-PTTPP

Fig. 2 shows the ^1H NMR of dichloro phosphorspirol. It can be seen that the chemical shift at δ = 4.2 ppm is according to the methylene ($-CH_2-$) of the hexahydirc ring (δ = 2.5 ppm for the solvent peak). Combining with the results of the infrared spectrum and NMR, it indicates that the dichloro phosphorspirol is synthesized successfully.

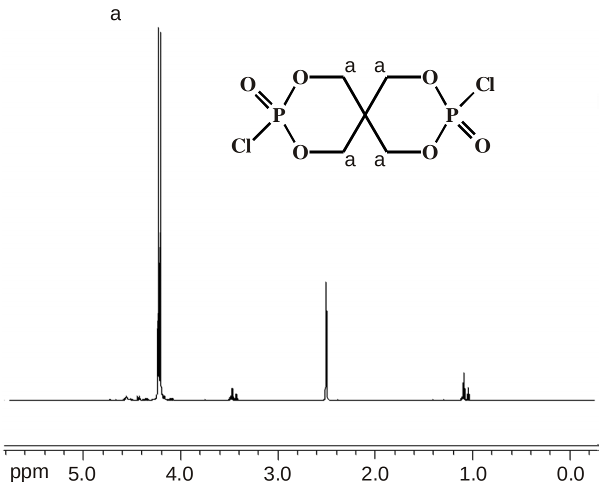


Fig. 2. ^1H NMR spectrum of dichloro phosphorspirol

Fig. 3 shows the ^1H NMR of the phosphorus-containing copolyester (PTT-PTTPP). There are four types of proton hydrogen. aH, δ = 8.25 ppm, is the proton hydrogen of the phenyl; bH, δ = 4.2 ppm, is the proton hydrogen of $-CH_2-$ of dichloro phosphorspirol; cH, δ = 2.5 ppm, is the proton hydrogen of $C-CH_2-C$ in the polymer backbone chain; dH, δ = 4.83 ppm, is the proton hydrogen of $-CH_2-O$ in polymer backbone chain. Combining with the results of FTIR and ^1H NMR, the synthetic copolymer has the following structural formula shown in **Scheme-I**.

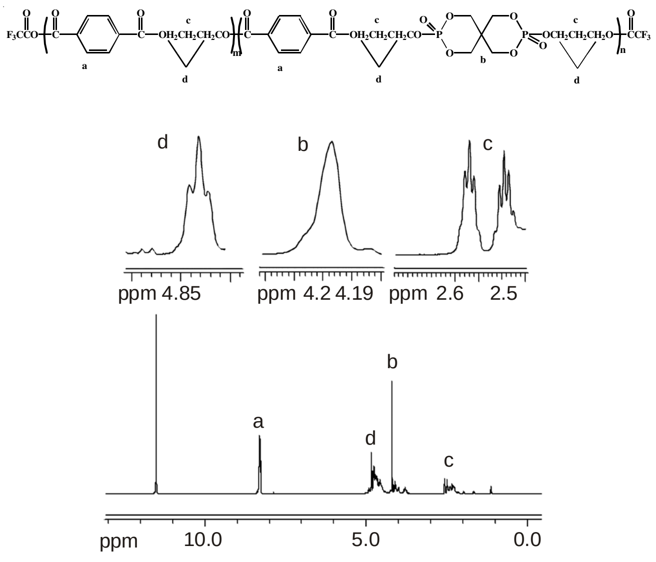


Fig. 3. ^{1}H NMR spectrum of PTT-PTTPP copolymer

Intrinsic viscosity and molecular weight: The intrinsic viscosity of PTT-PTTPP containing different content of phosphorus were measured and listed in Table-1. The average molecular weights (M_w) of the copolymers were calculated according to the eqn. 1 and listed in Table-1. With the increasing phosphorus contents, the M_w of the copolyester gradually decreased; it may be caused by the rigid molecular structure of HDPPE that is less active in the reaction. In the copolymer, if the polymerization degree of PTTPP block, *n*, is set as 1, according to the integral area results of different ^{1}H calculated from the ^{1}H NMR spectrum, the average polymerization degree of PTT block, m, is calculated and listed in Table-1. As the phosphorus content increases from 0 to 6.8 %, *m* decreases from 205.5 to 2.2 with decreasing $M_{PTT\text{-}b}$ from 38218 to 410 g/mol.

TABLE-1
INTRINSIC VISCOSITY AND
MOLECULAR WEIGHT OF PTT-PTTPP

P (%)	[η] (dL/g)	M_w (g/mol)	m	$M_{PTT\text{-}b}$ (g/mol)	n	$M_{PTTPP\text{-}b}$ (g/mol)
1(0)	0.653	38218	205.5	38218	-	-
2(3.0)	0.596	34817	8.4	1565	1	502
3(4.1)	0.517	30115	5.4	1010	1	502
4(5.4)	0.495	28807	3.5	646	1	502
5(6.8)	0.443	25723	2.2	410	1	502

Thermal stability: Fig. 4 displays the TG curves of different copolyesters and pure PTT and TG parameters were listed in Table-2. As seen in Fig. 4 and Table-2, the initial degradation temperatures ($T_{5\%}$) and the maximum degradation rate temperatures (T_{max}) of the copolyesters decrease with increasing phosphorus content, indicating that these copolyesters are less thermostable than conventional high molecular weight PTT, which is expected[15]. However, the char residues at 550 and 700 °C increase with increasing phosphorus content, suggesting that the phosphorus component can improve the flame retardancy of the copolyester.

TABLE-2
PARAMETERS OF TG CURVES FOR
PTT-PTTPP COPOLYMERS AND PURE PTT

Samples	$T_{5\%}$ (°C)	T_{max} (°C)	W_{550} (%)	W_{700} (%)
1(PTT)	354.1	402.6	2.54	0.01
2(3.0 %)	334.3	400.5	8.19	2.66
3(4.1 %)	332.2	388.9	14.60	5.38
4(5.4 %)	293.8	383.2	17.11	7.18
5(6.8 %)	273.4	362.1	18.84	8.58

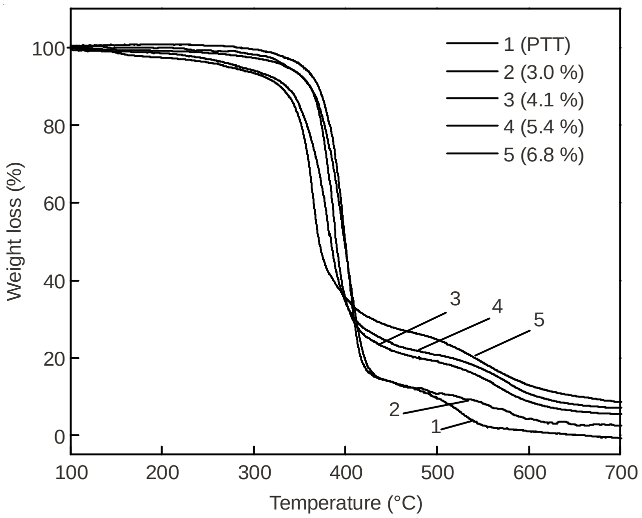


Fig. 4. TG curves of various PTT-PTTPP copolymers

Morphology of the combusted copolyester: Poly(trimethylene terephthalate) and phosphorus-containing copolyesters were emblazed at room temperature. When the PTT is burning, some droplets of molten PTT appear firstly and then a lot of smoke was released; while the phosphorus-containing copolyesters is burning, some droplets form and accompany with some bubbles. The morphology of the carbon layer after combustion of the phosphorus-containing copolyester and pure PTT were characterized by scanning electron microscopy, as shown in Fig. 5. The surface of the combusted PTT sample is relatively dense and smooth; while that of the copolyester sample shows many porous structures. Because the PTT-PP blocks contain some backbone segments of dichloro phosphorspirol that is an intumescent flame retardant, after high-temperature combustion, it generates phosphoric acid or polyphosphoric acid, which becomes a dense carbonized-layer on the polymer material surface. But phosphoric acid and polyphosphoric acid can promote polyester hydroxyl dehydration to generating the steam, thus the steam breaks the carbon layer in the diffusing process at high temperature, which leads to form microporous structure on the surface. The foamed carbonized layer prevents further combustion of the polymer.

Limiting oxygen index: The influence of the phosphorus contents on the limiting oxygen index of the copolyesters are shown in Table-3. In Table-3, PTT has the lowest limiting oxygen index among these samples, while the limiting oxygen index of the copolyesters increases with increasing phosphorus contents. Thus, the copolyesters have good flame retardancy, especially for the copolyester with 6.8 % phosphorus.

Conclusion

Block copolyesters containing different phosphorus contents were prepared by melt polycondensation method and their thermal properties were investigated. The results

TABLE-3
LIMITING OXYGEN INDEX OF
PTT AND PTT-PTTPP COPOLYESTERS

Samples	Limiting oxygen index (%)
1(PTT)	21.6
2(3.0 %)	26.1
3(4.1 %)	26.7
4(5.4 %)	27.1
5(6.8 %)	28.3

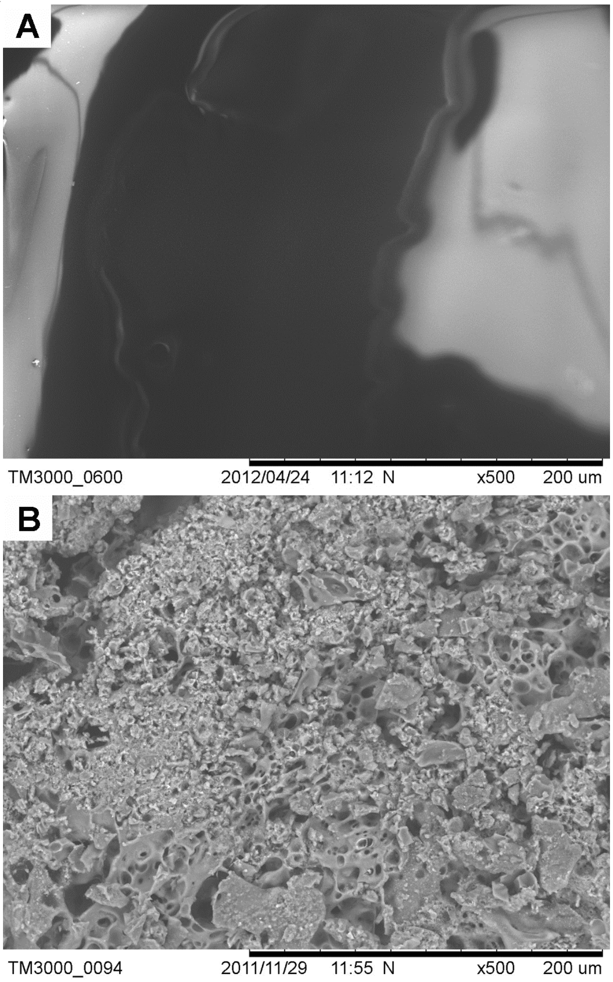


Fig. 5. SEM micrographs of the combusted surface of PTT and PTT-PTTPP samples

suggest that the copolyesters were synthesized successfully with proper content of phosphorus. The copolyesters have lower thermostability than that of pure PTT, but their char residues increase with increasing phosphorus content. The copolyesters show intumescent flame retardancy by forming foamed carbonized layer on the material surface to prevent further combustion. The limiting oxygen index of the copolyesters also increase with increasing phosphorus content.

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