

High Transmittance and Environment-Friendly Flame-Resistant Optical Resins Based on Poly(methyl methacrylate) and Cyclotriphosphazene Derivatives

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ABSTRACT: Highly transparent optical resins based on poly(methyl methacrylate) (PMMA) and two cyclotriphosphazene derivatives which acting as halogen-free flame retardants were prepared. The refractive indices, visible light transmittance, water absorption, flame-resistant characteristic, and the mechanical properties of the resins were studied. Comparing with pure PMMA, the as-prepared resins with the two additives exhibited higher refractive index (n_d), longer UV cutoff wavelength and better surface hardness. The water absorption of the resins was decrease with increasing of the additives. The visible light transmit-

tance of all the samples adding Additive A was higher than 90%. When the weight ratio of additive/MMA was 20/100, the limiting oxygen index (LOI) of the samples were 26 (with Additive A) and 22 (with Additive B), respectively. The surface hardness was increased from HB to 2H with increasing the content of the additives, and the impact and the tensile strength changed little for the formulas of the additives lower than 30% by weight. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 727–734, 2011

Key words: cyclotriphosphazene; PMMA; flame-resistant

INTRODUCTION

There is an increasing interest in the development of flame-resistant optical plastics. As one of the most popular plastics, poly(methyl methacrylate) is widely used in lighting fixture, optical glass and fiber, aerospace, advertising, and construction for its excellent transparency and weather resistance, good mechanical properties, light in weight, low cost, and easy to process. On the other hand, the performance of easily igniting and low surface hardness prevent it being used in certain commercial applications.¹ To solve the problems, two ways have always been used: one is the chemical incorporation of the flame-resistant species via copolymerization or using flame-resistant elements such as halogens and nitrogen containing groups to substitute the methyl group of the monomer. The other is the physical incorporation of flame

resistant additives, such as Sb_2O_3 , TiO_2 , and Fe_2O_3 , to provide improved fire resistance.^{2–5} However, the additives often reduce the optical and mechanical properties of PMMA. Specially, the metal oxides are often used in combination with halogen compounds to obtain the synergistic flame-retarding effect. Halogenated compounds will emit toxic and acidic fumes during combustion, which can choke people and potentially cause corrosion damage to equipment.⁶

In recent years, the use of halogenated flame retardant is extensively scrutinized by regulators and end-users⁷ for the foregoing reason. A number of halogen-free flame-resistant additives such as nitrogen-, phosphorus-containing^{8–12} organic compounds, and metal hydroxides^{13,14} have been widely researched for their environmental friendliness.

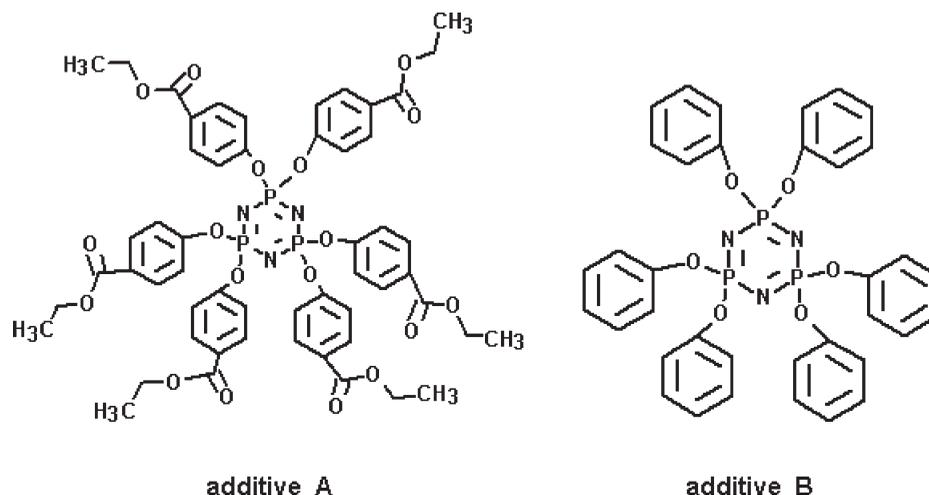
Among the phosphorus-containing compounds, the derivatives of cyclotriphosphazene have been evaluated in ABS resin,¹⁵ viscose rayon,¹⁶ PBT,¹⁷ polyurethanes,^{18,19} coating materials for wood,²⁰ polyimide resins,²¹ unsaturated polyesters,²² epoxy resin,^{23,24} and so on to improve the flame retardant properties of these polymers or natural products. We have also reported a novel reactive flame retardant hexa(allyl 4-hydroxybenzoate)cyclotriphosphazene and prepared a series of optical resins from the reactive cyclotriphosphazene and methyl methacrylate (MMA).²⁵

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Scheme 1 Molecular structure of the flame retardants.

In this study, we focus on the study of high transmittance and environment friendly flame-resistant PMMA without reducing its mechanical properties and thermal stability. First, hexachlorocyclotriphosphazene was reacted with phenol or ethyl *p*-hydroxybenzoate to synthesize two cyclotriphosphazene derivatives, respectively, to act as halogen-free flame retardant; and then, their flame-resistant effect on PMMA was examined; the optical properties and the mechanical strength of the cured resins were also studied.

EXPERIMENTAL

Materials

Hexachlorocyclotriphosphazene (HCCP) was synthesized in this laboratory as described in the literature.²⁵ Ethyl *p*-hydroxybenzoate and phenol were purchased from Sinopharm Chemical Reagent, China, and used without further purification. Potassium carbonate was purchased from Shanghai Zhanyn Chemical, activated at 140°C for 2 h. MMA, anhydrous sodium sulfate (Na₂SO₄), cuprous chloride (Cu₂Cl₂), and azobisisobutyronitrile (AIBN) were purchased from Sinopharm Chemical Reagent, China. MMA was purified by washing with a 5% aqueous sodium hydroxide solution and then with water, dried overnight with Na₂SO₄, distilled over Cu₂Cl₂ prior to polymerization. AIBN was recrystallized repeatedly from cold methanol and dried in a vacuum oven.

Synthesis of cyclotriphosphazene derivatives and polymers

Ethyl *p*-hydroxybenzoate derivative of cyclotriphosphazene²⁵ (m.p. = 88.8°C,) and phenol derivative of cyclotriphosphazene²⁶ (m.p. = 113°C) were synthe-

sized by reacting HCCP with ethyl *p*-hydroxybenzoate and phenol, respectively, using already reported methods. Scheme 1 shows the molecular structure of the two cyclotriphosphazene derivatives synthesized in this study.

A 50 g admixture of MMA and synthesized flame retardants according to certain proportion, 1 g AIBN were placed in a three-necked flask equipped with a stirrer, thermometer, and nitrogen inlet. The temperature of the reaction mixture was increased to 80°C and stirred for 0.5 h. Then, the preformed polymer was cast slowly into a glass-mold and placed in the vacuum oven, the temperature was kept at 40°C for 24 h, 80°C for 2 h, 100°C for 2 h and the oven was turned off. After the oven temperature was cooled to room temperature, the molds were removed and the colorless and sheet-like resins were obtained.

Instrumentation

The refractive indices (n_d) of the samples were measured by a WZS-IAbbé-Refractometer at 20°C. The visible light transmittance of the samples was measured by a S721 visible spectrophotometer at a wavelength of 550 nm. The ultraviolet-visible spectra of investigated resin sheets were recorded by a Shimadzu UV-2550 ultraviolet-visible spectrophotometer (Japan). The samples for above characterization were all prepared 3.0 ± 0.1 mm thickness.

The melt point was characterized by differential scanning calorimetry (DSC). DSC and thermogravimetric analysis (TGA) was performed on a synchronous thermal analysis instrument (STA 409 PC/4/H LUX, Germany) with nitrogen as the purge gas at a 10°C min⁻¹ scanning rate from 40 to 900°C. The morphology of the cyclomatrix resin and the solid residue after pyrolysis were observed on a FEI Sirion 200 field emission scanning electron microscope (Holland).

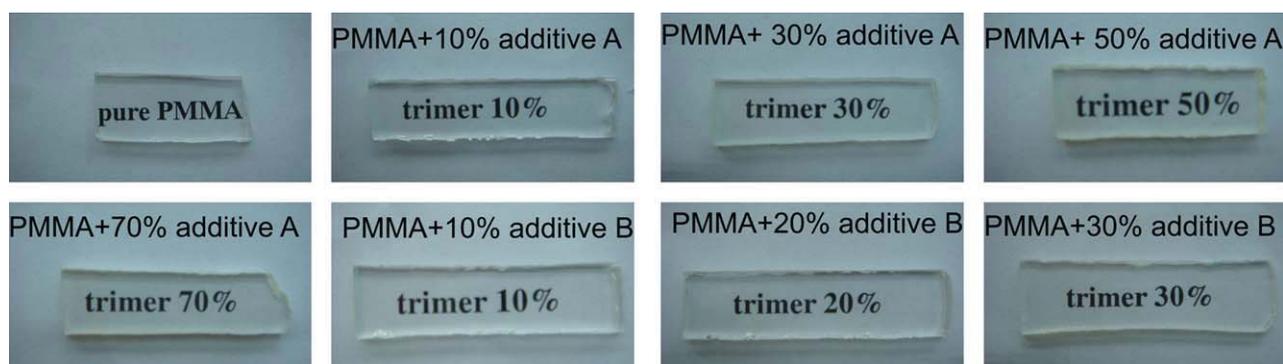


Figure 1 Photographs of pure PMMA and PMMA containing additives. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The tensile strength of the samples was measured using a universal test machine GP-TS2000S (Gaoping Testing Equipment, China) according to ASTM-D638. The impact strength of the samples was measured using an impact test machine XJU-22 according to GB/T 1843-1996 (Plastics-Determination of izod impact strength). The LOI values were used to evaluate the flammability of the cured resins according to ASTM-D2863. The surface hardness of the samples was determined by pencil test GB/T 6739-1996 B-Method. The water absorption in water and at 75% relative humidity was determined by GB/T 1034-1998 (Plastics-Determination of water absorption). The water absorption at 75% relative humidity was determined by simulating constant humidity in closed container with ammonium sulfate saturated aqueous solution at 23°C.

RESULTS AND DISCUSSION

Optical characteristics

Figure 1 was the photographs of pure PMMA and PMMA containing additives (Additive A/MMA = 10/100, 30/100, 50/100 weight ratio; Additive

B/MMA = 10/100, 20/100, 30/100 weight ratio). All the samples containing Additive A showed excellent transparency and macroscopical homogeneity. The samples containing Additive B also showed good transparency when the dosage of Additive B was lower than 40 wt %.

The refractive index values (n_d) and the visible light transmittance of the cured resins with different additives were shown in Figure 2. The n_d of pure PMMA was 1.493, and its visible light transmittance at 550 nm was 93.5%. The n_d of the samples containing 10 wt % additives was over 1.50. With increasing ratio of the additives to MMA in the samples, the n_d increased gradually. The visible light transmittance did not decrease when the dosage of the additives was lower than 10% and decreased slightly when the dosage was higher than 10%. The visible light transmittance of all the samples containing Additive A was higher than 90% [Fig. 2(a)]. The similar result was obtained when the dosage of the Additive B was lower than 30 wt % [Fig. 2(b)]. The result was due to the fact that the two additives possess the higher n_d based on the $-P=N-$ construction of cyclotriphosphazene, which has the potential to generate high n_d because of the relatively high electron density.²⁷ Additionally, the

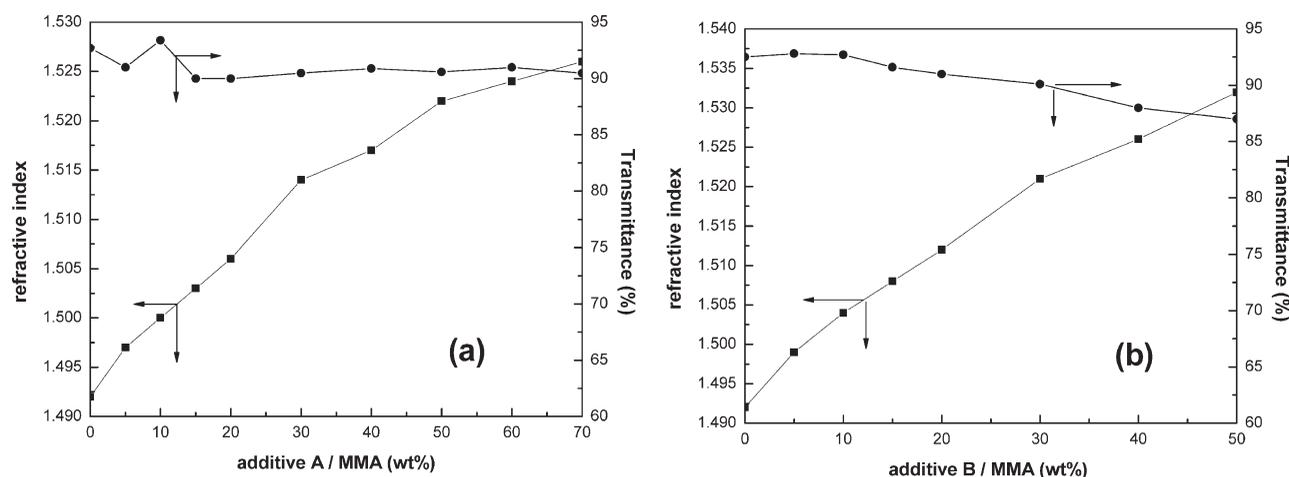


Figure 2 The effect of the ratio of additives to MMA on the refractive indices and the transmittance of the samples.

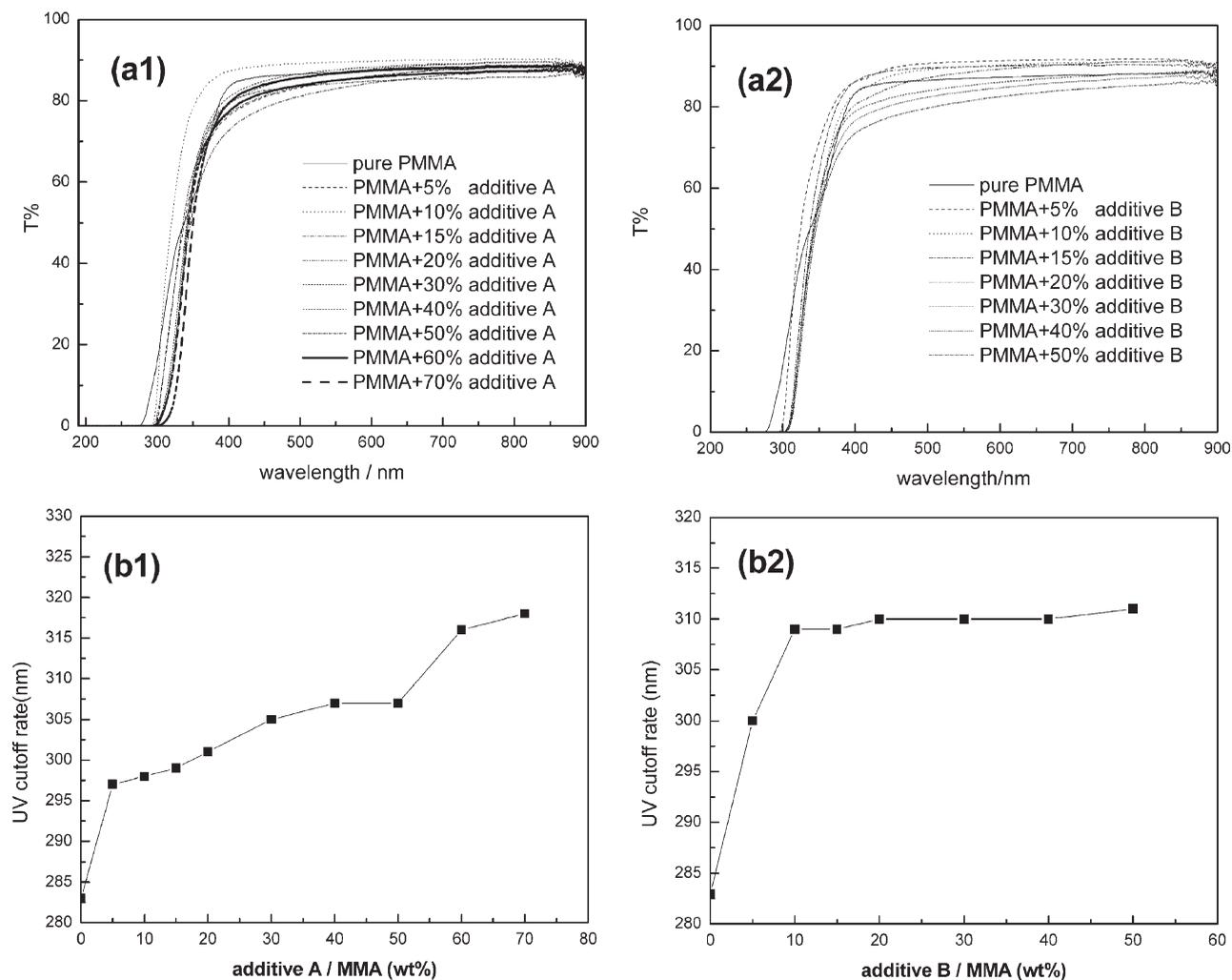


Figure 3 The Ultraviolet-visible Spectra (a1, a2) and UV-cutoff rate (b1, b2) of investigated resin sheets containing Additive A and B.

construction unit of cyclotriphosphazene is optically transparent in the region between 220 and 800 nm because the skeletal bonding structure in phosphazenes is quite different from the situation found in electron-rich organic compounds.^{28,29}

The UV-cutoff rate of investigated resin sheets according to the ultraviolet-visible spectra was shown in Figure 3. As compared with the pure PMMA (UV-cutoff rate = 283 nm), the UV-cutoff rate of the investigated resins was improved by adding Additive A or B, which was higher than 300 nm when the dosage of Additive A and B was 20 and 5% weight ratio, respectively. This was due to the absorption of benzene ring in Additive A and B.

Water resistance

The relationships between the water absorption (W_a) of the samples and the time at 75% relative humidity and in water were shown in Figure 4. Either at 75% relative humidity or in water, the W_a of the samples increased with the time within 120 h, the W_a was nearly saturated

at 120 h. The PMMA without additives possessed the highest W_a . When the ratio of two additives to PMMA was increased, the W_a of the PMMA decreased, especially the dosage of the additives was less than 30 wt%. At the same dosage of the two additives, the PMMA with Additive B showed the lower W_a than that of the PMMA with Additive A. This was due to the fact that the cyclotriphosphazene additives contain the benzene rings, which are hydrophobic groups. The weight percent of the benzene rings in the formulas increased with the addition of cyclotriphosphazene additives, resulting in the decrease of water absorption of the samples. Additive B contains the more benzene rings by weight percent than that of Additive A, the latter has the *para*-substituted ester group on the benzene ring.

Thermal stability of cyclotriphosphazene derivatives

The thermal stability of the cyclotriphosphazene derivatives were tested under nitrogen gas using a thermogravimetry analyzer, comparing with PMMA

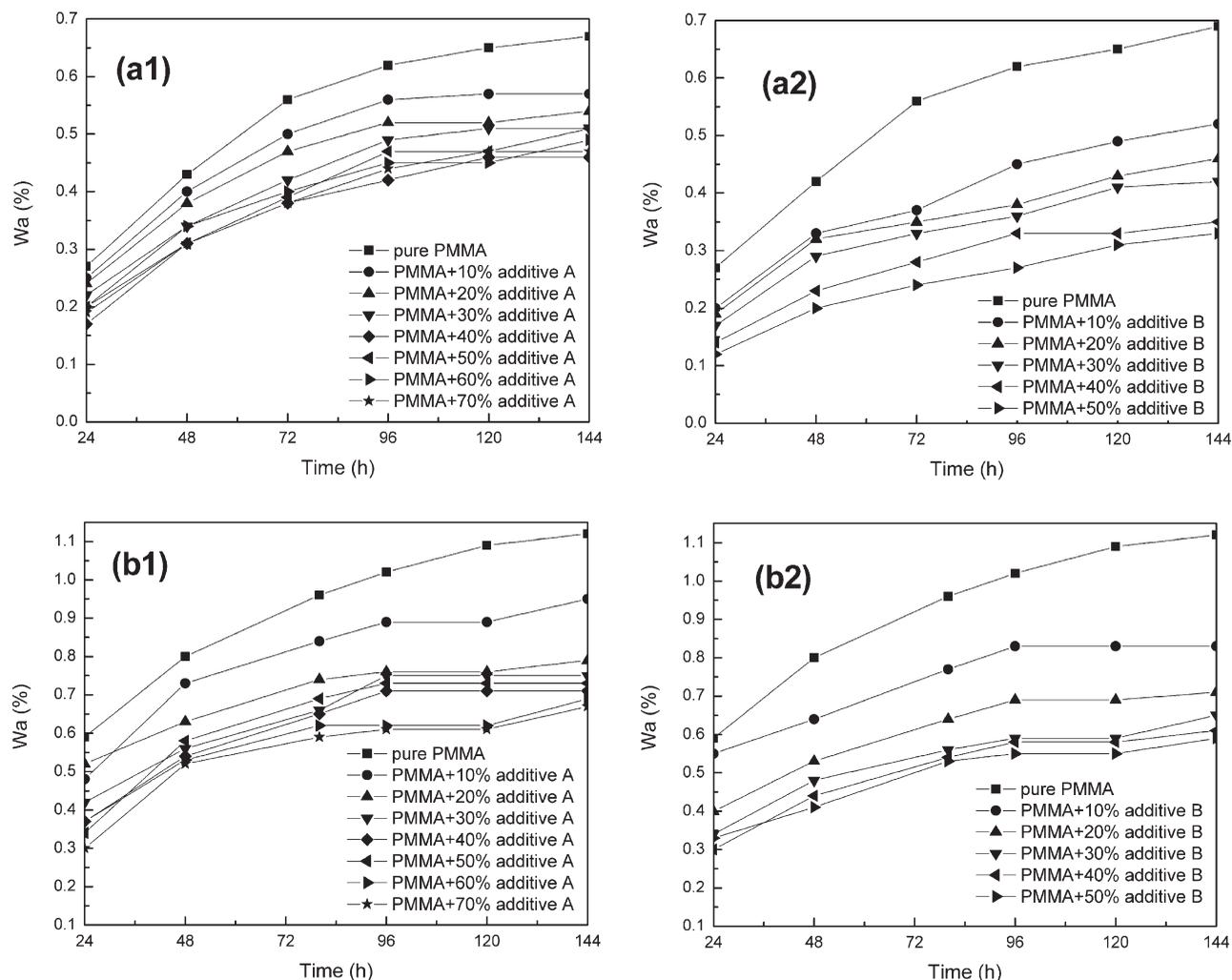


Figure 4 The effect of the time on the water absorption of the samples (a1 and a2) at 75% relative humidity; (b1 and b2) in water.

and the composite samples. The results were shown in Figure 5.

Both Additives A and B showed the higher thermal stability than PMMA and composite samples, abrupt mass reductions of the both additives were observed at ~ 345 and 376°C , respectively. The char residue of Additive A was 27% and that of Additive B was 1.92% at 900°C . A compound with a higher onset decomposition temperature and a considerable amount remaining in the TGA experiment at high temperatures can be considered as a good flame retardant.¹⁵ The onset decomposition temperatures of the two composite samples were similar to that of pure PMMA. While PMMA adding 30 wt % Additive A had 4.5% residue, PMMA adding 30 wt % Additive B had few residue at 900°C .

Flame retardant characterization

The flame retardants synthesized in this study were mixed with MMA at the ratio of 5–70 wt % to pre-

pare the PMMA sheets through bulk polymerization. The nonflammability of these samples was characterized using the LOI experiment. The results were shown in Figure 6. The LOI of the samples using 5 wt % of Additive A was over 20, while to achieve the same LOI, the 10 wt % of Additive B was required. In the cases using 20 wt % of the flame retardants, the LOI of those using Additives A and B were 26 and 22, respectively. When the dosage of additives was higher than 20 wt %, the LOI of those using Additive A increased gently but those of using Additive B increased rapidly. The LOI achieved to 28 at the 50 wt % of either Additive A or B.

The results showed that either Additive A or B can be used as a potential flame retardant for PMMA. The nonflammability of Additive A was better than that of Additive B. The reason for showing these results was that the two additives synthesized in this study have good thermal stability, and Additive A possesses the higher char yield than that of

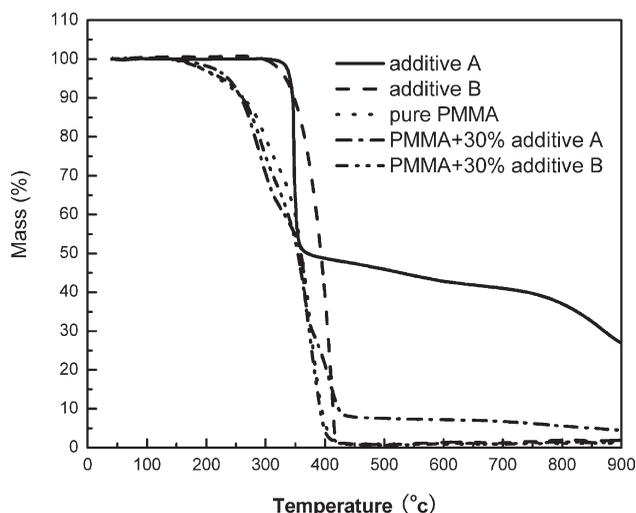


Figure 5 TGA curves of Additive A, Additive B, and PMMA in nitrogen.

Additive B after decomposition. Considering flame retardant, both good thermal stability and high char yield are beneficial to flame retardancy. UL-94 tests are still required to thoroughly evaluate the nonflammability. We will report the results in the subsequent article.

The morphologies and physical properties

The SEM images of fracture surfaces PMMA containing Additives A and B were shown in Figure 7. For either the PMMA adding 10 wt % Additive A or PMMA adding 10 wt % Additive B, SEM exhibited a homogeneous morphology in the micrometric scale, which was similar to that of the pure PMMA. Both PMMA adding 30 wt % Additives A and B showed a slight heterogeneous morphology. With the dosage of the two additives increasing in PMMA, the heterogeneous morphology became more and more obvious.

The effects of adding flame retardant on the mechanical properties of PMMA were examined. The results were listed in Table I. Comparing to the pristine PMMA, the surface hardness of the samples increased with adding the additives, while the samples with Additive B showed the higher values than those of adding Additive A. This was attributed to the rigid structures (cyclotriphosphazene and benzene ring) consisting in the two additives.

The results of impact strength and tensile strength in Table I showed that all the samples with the flame retardant compounds showed lower values than the pristine PMMA, especially the samples with Additive A. The reason was that the Additive A has a flexible chain on the each of benzene ring. In the case of the Additive B, the reduction in mechanical strength was lower than

Additive A. This was due to the more rigid structures of Additive B.

For Additives A and B, when the dosage of additive was higher than 30 wt %, both the impact strength and the tensile strength of the formulas decreased significantly. This was possibly attributed to the decreasing compatibility of additives with PMMA under high dosage (Fig. 7). On the other hand, the molecular chains of the PMMA prepared in this research are all linear. Future study will focus on resolving these problems by adding double functional acrylate monomer as crosslinking agent to prepare lightly crosslinking-PMMA composites and improve its impact and the tensile strength.

CONCLUSIONS

Two cyclotriphosphazene derivatives were synthesized by reacting hexachlorocyclotriphosphazene separately with ethyl *p*-hydroxybenzoate and phenol, and used as friendly flame retardants for PMMA. Compared with the pure PMMA, the samples concerning the additives showed increase of refractive indices from 1.497 to 1.532 and decrease of water absorption with increasing the content of the additives. The visible light transmittance of the samples was higher than 90% for all formulas concerning Additive A; the same results were obtained when Additive B was lower than 30% by weight in formulas. The nonflammability of the two flame retardants was characterized by LOI tests. In the cases using 20 wt % of the additives, the LOI of those using Additives A and B were 26 and 22, respectively. The mechanical properties were examined. The surface hardness was increased, and the impact and the tensile strength changed little for the formulas of the

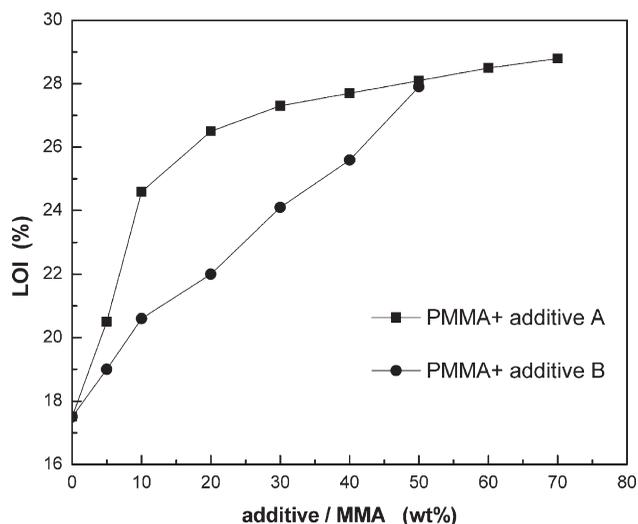


Figure 6 The LOI of PMMA containing Additive A and Additive B.

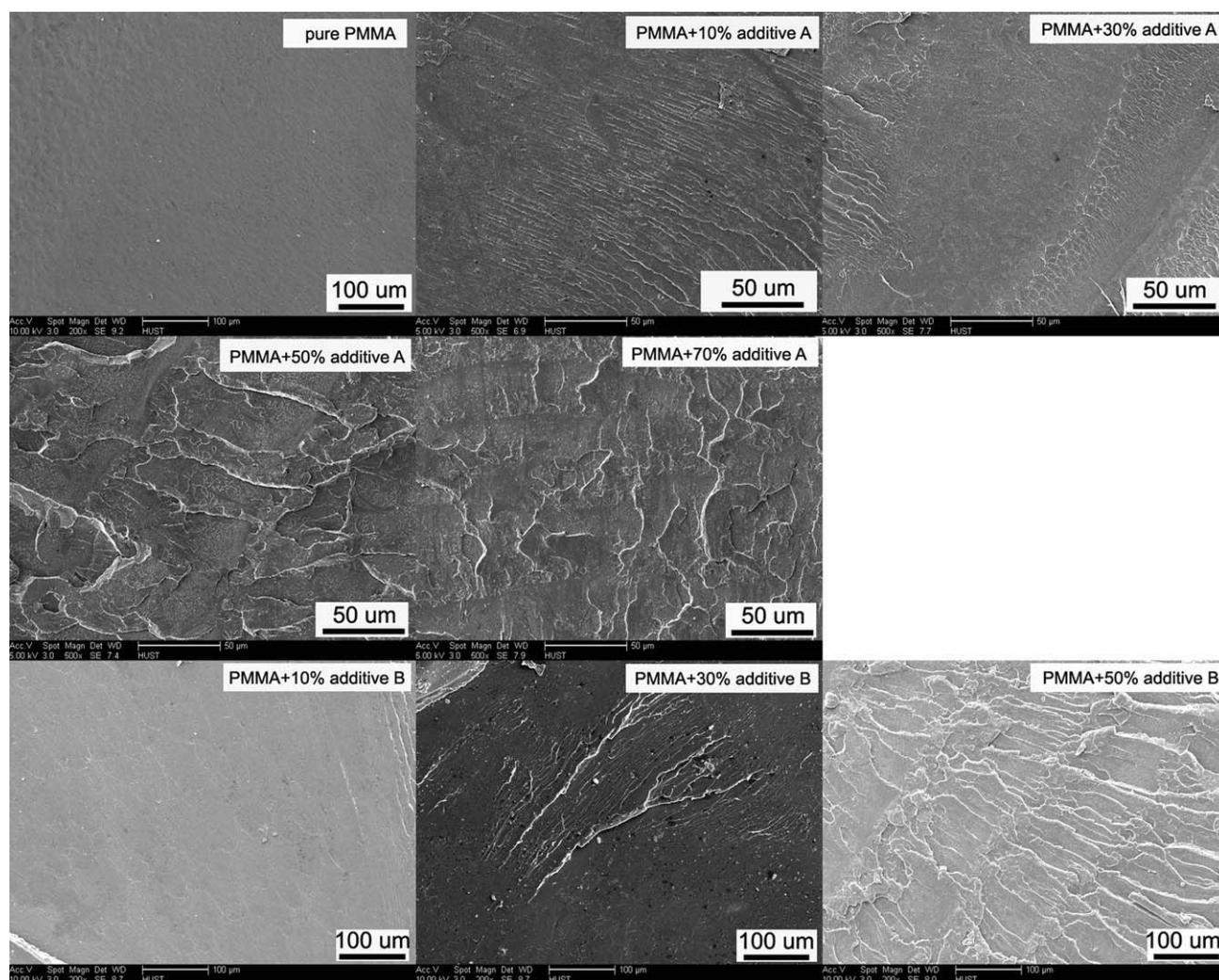


Figure 7 The SEM images of fracture surfaces of PMMA containing Additive A and Additive B.

additives less than 30% by weight. The results showed that either Additive A or B can be used as potential environment-friendly flame retardant for PMMA to obtain the incombustibility, the improved refractive index, low water absorption, and the high surface hardness, without reducing its transmittance and mechanical properties at low dosage. In our

future study, we will focus on preparing lightly crosslinking-PMMA composites to improve the mechanical properties, and give a full test of fire-retardant properties of the composites according to UL-94 method.

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TABLE I
Surface Hardness, Impact Strength, and Tensile Strength of PMMA with the Additives

Additive/MMA (wt %)	Additive A			Additive B		
	Surface hardness	Impact strength (kJ m ⁻²)	Tensile strength (MPa)	Surface hardness	Impact strength (kJ m ⁻²)	Tensile strength (MPa)
0	HB	8.73	52.8	HB	8.73	52.8
10	HB ~ H	7.14	38.0	HB ~ H	8.57	47.1
20	HB ~ H	6.00	37.3	H ~ 2H	8.21	42.2
30	HB ~ H	3.95	30.1	H ~ 2H	6.27	35.9
40	HB ~ H	3.91	26.8	H ~ 2H	5.59	22.9
50	H	4.19	21.7	2H	6.06	24.5
60	H	4.06	20.3			
70	H ~ 2H	4.37	21.2			

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